

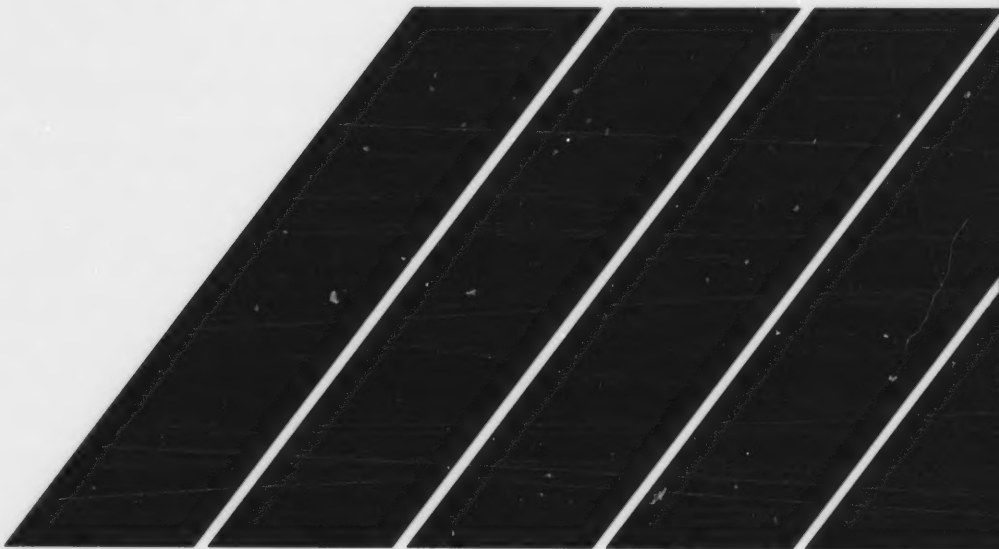
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**BIOMASS CONVERSION: THE INTEGRATION
OF THE STAKE PRETREATMENT AND THE
UdeS-SH PROCESS**

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EXECUTIVE SUMMARY AND OBJECTIVES

This report covers a 30-month research effort with the following objectives:

- to develop a generalized kinetic approach to steam/aqueous treatments of lignocellulosics;
- to derive operational rules to facilitate process and product control;
- to show, using a case study based on Populus tremuloides as a prototype hardwood, how to optimize the pretreatment in order to obtain maximum amounts of the three main constitutive fractions present in lignocellulosics;
- to determine optimum conditions for the enzymatic saccharification of the cellulose fractions;
- to present a discussion on avenues for lignin utilization as an important step towards commercialization of the pretreatment/fractionation approach proposed in this project;
- to show how pilot plant work can be effectively conducted in order to obtain significant data for commercial implementation.

The work reported shows that steam/aqueous treatments extend the thermo-mechano-chemical processes, common to the pulp and paper industry, into a region of high severity where rapid hydrolysis and even pyrolytic dehydration take place. The control of the hydrolytic and pyrolytic processes determines the destructureation, disaggregation and depolymerization patterns of the constitutive polymers, i.e. hemicelluloses, lignin and cellulose.

A unified kinetic treatment for the above processes requires the identification of key parameters (temperature, pressure, time and acid/base loading) as well as reaction engineering parameters (particle size of the feedstock, heat and mass transfer, solvolytic effects, fluidodynamic effects and possible side reactions due, for instance, to the presence of oxygen and leachates from reactor materials). We have proposed a simple phenomenological approach to describe conversion and yields during steam/aqueous treatments. The combination of temperature and time into a single parameter, i.e. the reaction ordinate (units of time, usually min.),

$$R_o = \int_0^t t * \exp[(T - 100)/14.75]$$

facilitates ordering of the data and permits rapid mapping of experimental conditions for optimum yields of recoverable polymers. Using R_o as the severity parameter we have shown, in Section A of this report, how to derive general operational rules to facilitate process and product control.

The specific application of our kinetic treatment has been conducted on a study aimed at the optimization of the fractionation of a prototype hardwood, Populus tremuloides. A pilot plant STAKE II unit having a maximum treatment capacity of 4 tonnes/h was used for this purpose. Our methodology and results, fully explained in Section B of this report, have shown:

- a maximum pentosan recovery of 65% of theoretical (based on the initial pentosans present in the untreated raw material) is obtained at $\log_{10}R_0 = 3.8$ without any additives. At higher severities, the recovered pentosans are lower than 65% due to degradation reactions. At lower severities the hydrolytic process is insufficient to reach the maximum pentosan recovery and the pentosans stay on the fiber;
- at $\log_{10}R_0 = 3.8$, lignin can be alkali- extracted. The recovery is 80% of total Klason lignin initially present in the untreated raw material;
- at $\log_{10}R_0 = 3.8$, the cellulose is quantitatively recovered although it has been partially depolymerized and needs bleaching to achieve its "natural" coloration;
- the enzymatic digestibility of the cellulose is close to theoretical after treatment severities beyond $\log_{10}R_0 \geq 3.2$;
- the overall results clearly suggest that steam explosion processes are fundamentally hydrolytic and they represent the extension into high severities of existing thermo-mechanical treatments.

The lignin derived from the pretreatment/fractionation approach is a thermoplastic material. STAKE Technology has conducted a survey of the existing literature, and they have presented in Section C of this report a number of options as possible uses of the derived lignin. The options are divided into two categories: low molecular weight chemicals, and polymeric lignin. The latter is further discussed in terms of uses in adhesives, as lignin plastics, as surfactant, as dye dispersant, as carbon black, as filler-binder for asphalt, as encapsulating agent for slow delivery and as a material having good properties in pelletization of ores. The development of these uses requires, according to STAKE Technology Ltd, the selection of specific targets guided by marketing opportunities, the development of expertise in the areas of characterization, derivatization and formulation of resins and plastics, and rapid tests of the products in the market place in order to know their acceptance and/or modifications needed to improve the product.

Finally, in Section D of this report, we present the details of the pilot plant facility located in Sherbrooke. The layout of the plant, its functionality and the improvements made to the system during the tenure of

the contract are fully described and assessed. The pilot plant has a multipurpose function to study in detail the many facets of thermo-mechano-chemical processes of which pretreatment/fractionation is a specific application.



RÉSUMÉ ET OBJECTIFS

Ce rapport couvre des travaux de recherche exécutés à l'intérieur d'une période de 30 mois et dont les objectifs étaient les suivants:

- . le développement d'une approche cinétique unifiée et générale pour les traitements aquo-vapeur des matières lignocellulosiques.
- . l'établissement de règles opérationnelles afin de faciliter le contrôle des procédés et des rendements et la qualité des produits issus des traitements.
- . exécuter, comme étude de cas, l'optimisation du prétraitement/fractionnement du Populus tremuloides, une essence prototype représentative des feuillus. Le critère d'optimisation était de trouver les conditions opératoires qui maximisent les rendements des trois fractions constitutives, i.e. les hémicelluloses, la lignine et la cellulose.
- . déterminer les conditions optimales pour la saccharification enzymatique de la fraction cellulosique.
- . présenter une discussion sur les directions les plus prometteuses pour la valorisation de la lignine. Cette valorisation est essentielle pour l'éventuelle commercialisation de l'approche prétraitement/fractionnement proposée dans ce projet.
- . montrer comment obtenir des données significatives au niveau commercial en travaillant à l'échelle pilote.

Les résultats obtenus montrent que les traitements aquo-vapeur étendent les procédés thermo-mécano-chimiques, couramment utilisés dans le secteur des pâtes et papiers, vers une région de haute sévérité où l'hydrolyse et les dégradations pyrolytiques ont lieu comme mécanismes prédominants. Le contrôle de ces mécanismes détermine le degré de déstructuration, de désagrégation et de dépolymérisation des fractions constitutives.

Un traitement cinétique unifié pour les traitements aquo-vapeur requiert l'identification des paramètres clé (i.e. température, pression, temps et concentration acido-basique) ainsi que les paramètres caractéristiques au niveau engineering (i.e. dimensions des particules du bois, transfert de matière et d'énergie, effets solvolytiques, effets fluidodynamiques et possibles effets périphériques dus, par exemple, à la présence ou non de l'oxygène de l'air et à la présence d'ions métalliques dérivés des parois du réacteur). Nous avons proposé une simple approche phénoménologique afin de décrire la conversion et les rendements des polymères constitutifs des matières lignocellulosiques pendant les traitements aquo-vapeur. La combinaison de la températu-

re et du temps dans un paramètre unique, i.e. la coordonnée réactionnelle

$$R_0 = \int_0^t t \cdot \exp[(T - 100)/14.75]$$

permet l'établissement de "cartes opérationnelles" qui facilitent trouver les conditions optimales pour la récupération des polymères constitutifs. En utilisant R_0 comme le paramètre décrivant la sévérité, nous avons montré dans la Section A du rapport comment établir les zones opérationnelles pour faciliter le contrôle des procédés et des produits.

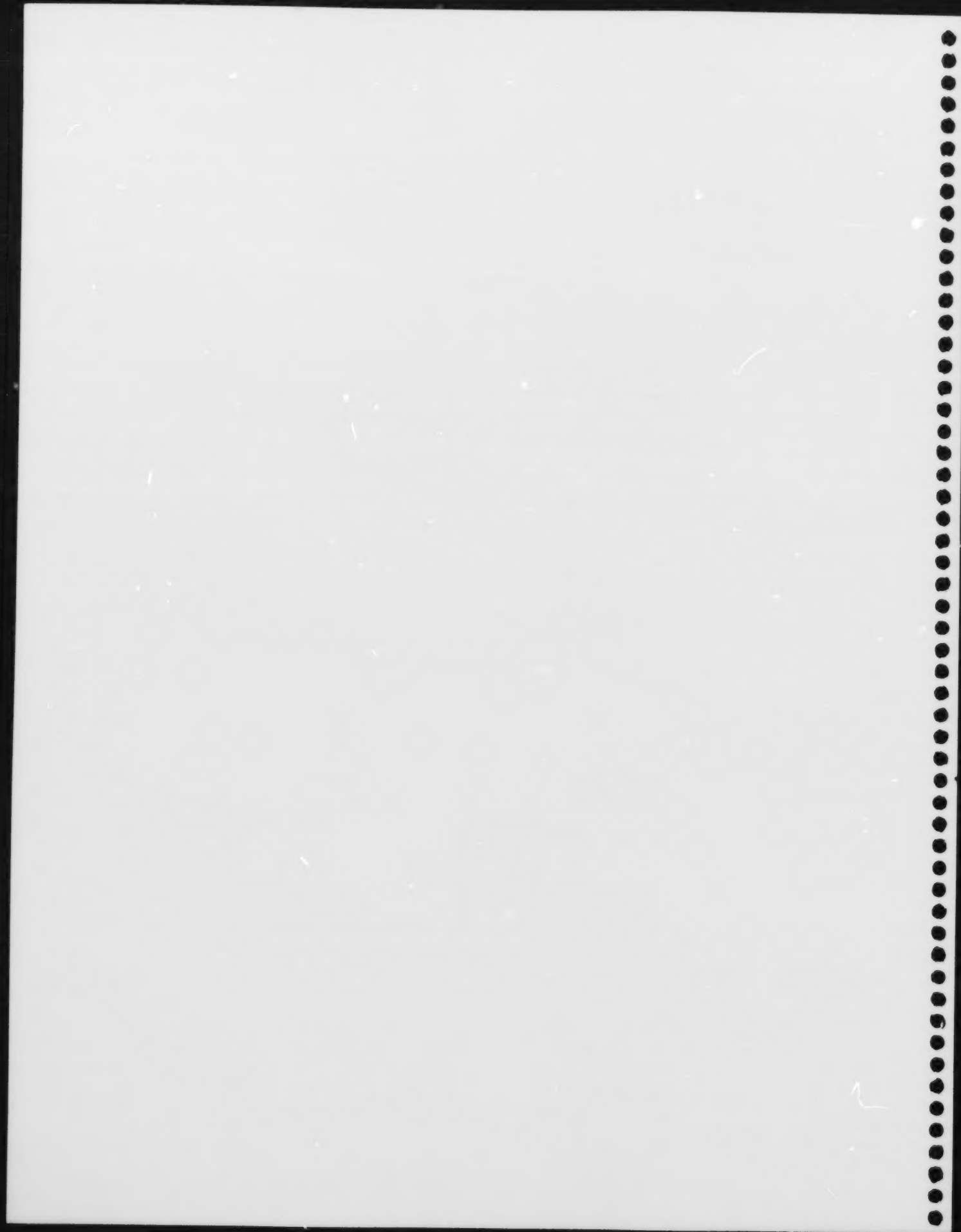
Comme application spécifique du facteur de sévérité, R_0 , nous avons effectué une étude de cas visant l'optimisation du fractionnement du Populus tremuloides, un feuillu prototype. Le plan pilote STAKE II, installé à Sherbrooke et ayant une capacité de 4 tonnes/h a été utilisé à cette fin. La méthodologie suivie et les résultats obtenus, présentés en détail dans la Section B de notre rapport, ont montré:

- . un rendement maximal possible en pentosanes équivalent à 65% du potentiel théorique est obtenu à des sévérités autour de $\log_{10}R_0 = 3.8$ sans addition d'acide ou de base. A des sévérités plus élevées, la dégradation des pentosanes force des rendements inférieurs, alors que, à des sévérités inférieures, la cinétique hydrolytique est trop lente pour atteindre le rendement de 65% et les pentosanes restent préférentiellement sur la fibre.
- . à $\log_{10}R_0 = 3.8$, un rendement d'environ 80% de la lignine Klason initialement présente dans le bois, est obtenu par voie d'extraction alcaline et précipitation en milieu acide.
- . à $\log_{10}R_0 = 3.8$, la cellulose initiale est récupérée intégralement. Elle se trouve toutefois partiellement dépolymérisée et requiert du blanchiment afin d'obtenir la couleur "naturelle".
- . la digestibilité enzymatique de la cellulose est près du maximum théorique après traitements à des sévérités $\log_{10}R_0 > 3.2$.
- . les résultats considérés globalement suggèrent clairement que les procédés aquo-vapeur sont essentiellement hydrolytiques et qu'ils représentent une extension, dans le domaine de plus hautes sévérités, des traitements thermomécaniques existants.

La lignine dérivée du procédé est thermoplastique. STAKE Technology Ltd a effectué une analyse de la littérature et a ajouté leur propre expertise corporative afin de présenter, dans la section C de ce rapport, des options valorisantes pour la lignine. Ces options peuvent se diviser en deux catégories de marchés: produits chimiques de faible poids moléculaire et applications de la lignine en tant que polymère.

Ce dernier marché est discuté par voie de ces applications: dans les adhésifs, comme plastique, comme surfactant, comme agent dispersant, comme matière première pour la préparation de noir de carbone, comme composant des asphaltes, comme agent d'encapsulation et comme agent pelletisant. Le développement de ces applications requiert, selon STAKE Technology Ltd: le choix de cibles spécifiques en fonction d'opportunités des marchés présents et futurs, la mise en oeuvre d'une expertise dans le secteur de la caractérisation avancée, la dérivatisation de la lignine et sa formulation dans des résines et des plastiques ainsi que des essais multiples avec les différents utilisateurs afin de connaître l'acceptabilité des nouvelles formulations ainsi que les modifications les plus appropriées visant l'amélioration des produits.

Finalement, dans la Section D du rapport nous présentons en détail l'installation pilote construite à Sherbrooke autour de la technologie STAKE II. La disposition des équipements, leurs fonctions et les améliorations apportées au cours des travaux relatifs à ce contrat sont discutées. Le plan pilote est une installation unique en Amérique du Nord ayant une multiplicité de fonctions et possibilités d'étude des procédés thermo-mécano-chimiques avancés parmi lesquels le prétraitement/fractionnement est une approche particulière.



SECTION A: PHENOMENOLOGICAL KINETICS AND REACTION ENGINEERING
ASPECTS OF STEAM/AQUEOUS TREATMENTS

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ABSTRACT

Thermo-mechano-chemical treatments of lignocellulosics are well known processes used commercially in the production of high yield pulps. When conducted at high severities, steam/aqueous treatments extend the thermo-mechano-chemical processes into a region where rapid hydrolysis and even pyrolytic dehydration take place. Their control determines the destructurement, disaggregation and depolymerization patterns of the constitutive polymers.

A unified kinetic treatment for the above processes requires the identification of key parameters (temperature, pressure, time and acid/base loading) as well as reaction engineering parameters (particle size of the feedstock, heat and mass transfer, solvolytic effects, fluidodynamic effects and possible side reactions due, for instance, to the presence of oxygen and leachates from reactor materials).

We have proposed a simple phenomenological approach to describe conversion and yields during steam/aqueous treatments. The combination of temperature and time into a single parameter, i.e. the reaction ordinate, facilitates ordering of the data and permits a rapid mapping of experimental conditions for optimum yields of recoverable polymers. Using this severity parameter we have derived operational rules to facilitate process and product control.

INTRODUCTION

Pretreatment of lignocellulosics to induce destructuring and disaggregation is the basis of the pulp and paper industry, the fiberboard sector and more recently the hydrolytic approaches to yield pentoses and/or hexoses. As well, the fractionation of lignocellulosics, to obtain each of the major components (extractives, hemicelluloses, lignin and cellulose) in maximum yield and purity, relies on an appropriate pretreatment technology capable, furthermore, of processing residual lignocellulosics such as straws, bagasse and hardwood residues. The latter are

available either as products of the forest operations or the transformation industries. The fractionation of softwood residues is not as well established probably due both to their structural configuration and chemical linkages which require the use of additives (SO_2 or inorganic acids are common additives) acting essentially as catalysts.

The basic structural model for lignocellulosics is well described in textbooks (Sjostrom, 1981¹; Fengel and Wegener, 1984²). The key features can be summarized as follows: a middle lamella, comprised essentially of lignin and hemicelluloses, glues together the cell layers within which cellulose, the predominant component, is bundled together as composite microfibrils having regions of amorphous cellulose separating blocks of crystalline polymer. Hemicelluloses and lignin are present between microfibrils and help to maintain the microfibrils together to form an individual fiber.

The primary goal of the pretreatment is to reduce the complex structural system, described above, to a destructured state in which individual fibers are separated. Furthermore, if the severity of the treatment is high enough, further destructuring at the level of the fibrillar substructures takes place.

Goring (1963)³ showed that the anhydrous glass transition temperatures of isolated hemicellulose and lignin are between 130-190°C and that water has a plasticizing action which reduces the softening temperatures of both polymers to about 100°C or less. The thermal behaviour depends then on the combined effects of temperature and moisture, particularly in the amorphous zones (Back and Salmen, 1982)⁴. In the Asplund process, in which pressurized steam refining is used at or above 160°C to produce fiber board with minimum mechanical energy (around 200 Kwh $\cdot$ t⁻¹), the significant point is to reach a temperature at which relatively low mechanical energy input is required to defibrate due to the softening of the middle lamella (Back and Salmen, 1982)⁴. Higher mechanical energies are needed when the softening of the middle lamella is not well developed as in the case of pretreatments at 120-130°C where the mechanical energy needed to defibrate is as high as 1 MWh $\cdot$ t⁻¹.

Evidence for structural changes related to the softening of the middle lamella components during steam treatment and particularly the lignin was provided by Marchessault and St-Pierre (1980)⁵ who observed that lignin in the pulp residue had coalesced into small spherical globules of less than 5-10 μm diameter. This was a direct experimental indication that after the softening (and perhaps melting) transition, the lignin polymer nucleates in small globules leading to thermoplastic spheres when cooling.

The essential point to be derived from the above discussion is that temperature, moisture and mechanical energy are required to induce

destructuring of lignocellulosics. This destructuring effect, which we have, so far, discussed in terms of physical mechanisms, may also be accompanied by chemical changes which affect both ultrastructure and functionalities of the constitutive polymers.

The chemical consequences of thermal treatments of lignocellulosics either as a suspension (large amounts of liquid present) or as a steaming process (low amounts of free water present) can be summarized as follows (Overend and Chornet, 1987)⁶:

- disaggregation of lignin-carbohydrate complexes. The extent of disaggregation is a function of the severity of the treatment. The net result is the possible recovery of rather pure hemicellulose, lignin and cellulosic fractions;
- rupture of glycosidic bonds essentially due to a hydrolytic mechanism. Such an effect is evidenced in both hemicelluloses and cellulose polymers where their degrees of polymerization are functions of severity (Puls et al., 1985)⁷;
- extensive cleavage of C-O-C bonds: (1) those related to β -O-4 linkages in lignin (Robert and Bardet, 1985)⁸; (2) those related to methoxyl groups in lignin (Chua and Wayman, 1979)⁹;
- depolymerization of lignin down to relatively small subunits of around 2000-3000 mass-average molecular weight values (Chum et al., 1985)¹⁰; Glasser et al., 1983¹¹);
- high crystallinity in the residual cellulose until very intense treatment severities result in pyrolytic dehydrations (Marchessault et al., 1983)¹²;
- significant resistance to deacetylation (Puls et al., 1985)⁷. Recent work by Bouchard et al.¹³ has shown that deacetylation takes place preferentially on the solubilized fragments rather than in the solid phase.

The presence of acid/base catalysts during pretreatment and, as well, the use of organic solvents clearly must affect both the physical and chemical changes of the constitutive polymers. It is well known that acid/base catalysis is essential in chemical pulping and has a definite influence in delignification kinetics. The role of organic solvents is to improve the solubilization of lignin, based essentially on the thermodynamic affinity between the polyphenolic structure of lignin and the solvent. That the solvent also acts as a plasticizer, lowering the glass transitions of the constitutive polymers, is a distinct possibility which would result in decreased mechanical energies for defibration.

Having established that pretreatment involves a combination of physical (destructuring and disaggregation) and chemical modifications

(depolymerization and overall C-O-C cleavages) we shall now focus on two major objectives: (a) to position steam-explosion as a particular category of thermo-mechano-chemical processes; and (b) to describe how a simple severity parameter, combining time and temperature can be used to follow specific structural and chemical changes in steam/aqueous treatments.

THERMO-MECHANO-CHEMICAL OPTIONS

Processes combining thermal, mechanical and chemical effects can be traced back to the early patents of Mason (1929)¹⁴ and Babcock (1932)¹⁵. Mason described an equipment, known as the Masonite gun, which was developed to contact saturated steam with wood chips or shavings for a short period of time followed by sudden release of the steamed material through a discharge valve which is rapidly opened. Babcock proved that the above concept led to fermentable sugars whereas Mason applied the concept to defibration and board production.

The patents of Mason and Babcock clearly suggest that a thermal treatment with steam leads to condensation of steam and the formation of a wetted (i.e. aqueous) mass of lignocellulosics. Hydrolysis can thus occur if temperature is high enough to enhance, thermodynamically, the dissociation of liquid water and thus create a highly ionic milieu lowering the energy barriers for hydrolysis. The accessibility of steam into the inner structures of the lignocellulosics is warranted since vapour phase diffusion is orders of magnitude higher than liquid phase diffusion. Thus one can conceive that the penetration of steam happens first and its condensation produces the "liquid water" present inside the "capillary-like" microporous structure of lignocellulosics. The "wetted" material is driven at high velocities through the nozzle by sudden opening of the discharge (i.e. blow-down) valve. The water present within the capillaries is, before the discharge, at high temperature in equilibrium with the high pressure present in the gun. Since the low pressure side of the discharge valve is normally 101.3 kpa the water (and with it the solid substrate!) cools rapidly to 100°C by evaporation forcing, literally, an explosion whose mechanical effect is extensive defibration, some defibrillation and some rupture of the fibers probably along weak zones of highly amorphous cellulose.

The mechanical effect, in the above processes, is clearly caused by the sudden evaporation of the "inner water". Since the net result is the separation of fibers one can envisage that the evaporation of water generates high shear forces between the "cylindrical tubes" known as fibers. Since the "glue" between the fibers, i.e. the middle lamella, is with all probability at a temperature beyond the glass transitions of both lignin and hemicellulose, the high shear forces cause the sliding and separation of the "cylindrical tubes" (i.e. the fibers). A second possible mechanical effect was implied by Mamers and Rowney's 1979 patent¹⁶ who, by adding an inert gas at very high pressures inside the reactor to

drive the steamed lignocellulosics through a set of specially designed bars, provided evidence of a shear effect caused by the high velocities through the exit nozzle. This suggests that some polymeric changes may occur due to shear and/or ultrasonic effects related to the passage through the nozzle.

The importance of the above discussion is that it positions the steam explosion process as a thermo-mechano-chemical process in which the combined presence of heat (as steam), mechanical forces (shear effects) and chemistry (as hydrolysis) results in massive disruption of the lignocellulosic structure. A further point shown above is that the presence of liquid water coming from initial moisture and, above all, steam condensation, is essential for the destructuring to occur.

Can thermo-mechano-chemical effects also take place in the presence of large amounts of liquid water? The question is of importance since finely divided lignocellulosics (i.e. sawdust) cannot be adequately handled by Mason derived technologies either due to limitations on heat and mass transfer within the reactor or to the difficulties inherent to separating finely divided wet solids from a vapor/gas stream. For these reasons, as well as for the simplicity of their operation, the treatment of aqueous suspensions is of interest.

The thermo-chemical studies of Bobleter and co-workers¹⁷⁻²⁰ on lignocellulosics have provided key experimental evidence that water alone, at high temperatures, could be responsible for extensive hydrolysis and solubilization of the carbohydrates as well as the low molecular weight fractions of the lignin. The "hydrothermolysis" process described by the authors, and based on percolation technology, has shown that, at temperatures comprised between 150 and 360°C, lignocellulosics can be degraded to soluble products. In the case of aspen (*P. tremuloides*) solubilisation maxima at 180, 270 and 340°C were observed for hemicellulose, cellulose and lignin respectively. The nominal residence time of the aqueous phase in the hot zones of the percolator was shown to have a definite influence in product yields and quality suggesting that hydrolysis mechanisms both in the heterogeneous (wood/liquid) and homogeneous (liquid-only) phases are responsible for the observed results.

Mechanical effects are known to affect the hydrolysis of complex polysaccharides. Key evidence exists from work on starch suspensions. In a process described by Hughes (1979)²¹ it is indicated that when heated starch suspensions are subjected to a compression-decompression cycle such as it will happen in a fixed capillary or orifice the energy released in the decompression zone induces structural changes which enhance the hydrolytic rates. The initial concept leading to Hughes¹ patent can be traced back to Schutze (1924)²² who was the first author, in our knowledge, to provide evidence of aqueous-phase hydrolysis of starch being enhanced by flashing the suspension through an orifice. Hughes' interpretation and contribution, fifty five years later!.

was to recognize the possible effect of the energy liberated upon sudden decompression through an orifice. Whether this energy is transmitted to the polymer through shear effects (via, for instance, ultrasonic cavitation) or localized heat dissipation (thus increasing the local temperatures of the polymer) is unknown and was not discussed by Hughes. In a recent paper we have shown quantitatively how the hydrolysis of dextrans is enhanced, within a definite molecular weight range, by passage of the dextran suspension through a homogenizing valve (Carrasco et al. 1988)²³. Thus a mechanical effect was experimentally confirmed. Whether the enhancement was due to bond activation or simply, and most likely, to increased accessibility of the acid catalyst induced by shear destructuring of the dextran matrix, is unknown.

The application of shear destructuring to lignocellulosics has been illustrated in two distinct pieces of work: (a) Turbak et al. (1983)²⁴ showed that passage through homogenizing valves profoundly changed the microstructure of cellulose. Gel-type compounds were thus developed. This is a clear indication of structural modifications induced by shear-like effects; (b) more recently, Kamide and Okajima (1987)²⁵ have shown that when aqueous suspensions of cellulose, up to 10% solids consistency, are treated for very short times at high temperatures (~250°C) and suddenly released by opening a discharge valve, the cellulose undergoes structural changes. They were able to identify these as H-bonding modifications probably induced by structural H-bond changes or shifts due to enhanced water penetration in between adjacent cellulose molecules. This effect was implicitly attributed by the authors to the sudden decompression since direct exposure to 250°C without decompression did not lead to structural changes.

The preceding paragraphs in this section illustrate the point that steam/aqueous treatments at elevated temperatures, typical of so-called "explosion" and "hydrothermolysis" processes, are essentially hydrolytic in nature and that the effect of the sudden decompression is essentially a mechanical effect which induces ultrastructural changes and, in aqueous suspensions, may force increased solvation as a step towards H-bonding changes in the cellulose. The exact mechanism of the mechanical effect is not known but flash evaporation of water retained in the capillaries of the substrate, as in the steam-explosion processes, and cavitation sonic effects, in the liquid-phase treatment, are likely to be the initial triggering causes for the structural effects. Support for the sonic-based mechanism can be found in the work of Colvin (1976)²⁶.

As a summary, steam-explosion and aqueous-phase treatments to destructure lignocellulosics are essentially thermo-hydrolytic-mechanical processes and as such we can categorize them as thermo-mechanical vapor and aqueous/vapor treatments. Our abbreviated terminology will thus name these processes TMV and TMAV, respectively.

When an organic solvent is present with or instead of the aqueous medium, then our terminology will name these processes thermo-mechano-solvolytic or TMS. The latter cover both the vapor treatments (essentially a solid-vapor system) and the liquid/vapor treatments (or liquid-phase slurry systems). Little is known about solvolytic systems subjected to mechanical effects. The organosolvent pulping processes proposed as alternatives to the current aqueous based processes have been investigated at long residence times in batch reactors without the added feature of sudden decompression. A recent summary on the area has been published by Johansson et al. (1987)²⁷. The relatively abundant literature on the subject points to the high quality of the cellulosic pulp obtained by different organosolvent combinations as well as the recovery of a "pure lignin" fraction. The objective of fractionation is thus clearly achieved via organo-solvent treatments. Application of rapid thermo-mechanical technologies could facilitate both solvent penetration, thus improving the solubilization of the hemicelluloses and lignin, and defibration of the substrate. Evidence for the latter effects has been published based on the results obtained in our laboratory (Vanasse et al. 1988)²⁸. The use of the TMV technology (or steam-explosion) adapted to organic solvents deserves due consideration although it will require careful engineering design to avoid vapor and liquid losses.

TMV or steam-explosion technologies

(a) Batch processes. The Masonite gun type technology is the basis of these processes which were first described as having potential for fractional separation of hemicelluloses, lignin and celluloses in a patent by Delong (1981)²⁹ and a paper by Marchessault et al. (1983)¹². Further patents covering detailed modes of operation and specific operating conditions were attributed to Delong (1983)³⁰ and Foody (1984)³¹. A variant of the steam explosion process specifically adapted to the pulping of non-wood species is known as the Siropulper (Mamers et al. 1981)³².

(b) Continuous processes. They are based on a high pressure feeding system, followed by a digester equipped with a transfer screw, and a blow-down valve which acts as an orifice. Conventional feeders used in the pulp and paper or fiberboard industries had been unable to achieve trouble-free feeding against the high steam pressures needed in the steam-explosion processes. This situation changed with the development of a patented coaxial reciprocating feeder (Brown, 1981³³; Brown and Bender, 1981)³⁴. The residence time of the fiber material through the digester is controlled by the characteristics of the rotating transfer screw and the opening sequence of the feeder choke cone and the discharge blow valve. The present STAKE II system with a 25.4 cm feeder is capable of treating 100 kt a^{-1} of biomass feedstock.

TMAV or aqueous technologies

The development of these processes has been limited, so far, to the treatment of finely divided lignocellulosics having 10^{-3}m as typical dimension. A continuous unit capable of treating up to 1 kg min^{-1} of medium consistency slurries ($\sim 15\%$ wt solids) is in operation in our laboratory. The unit was initially described by Koeberle et al. (1985)³⁶. The batch autoclave work leading to the design of a continuous system has been documented by Rubio Torres et al. (1986)³⁵. An extensive optimization study on the fractionation of Populus deltoides has been completed (Bouchard et al.¹³). In our technology, the mechanical defibration and defibrillation is effected by passage of the slurry, at temperatures greater than 160°C , through a homogenizing valve operating with pressure differentials of 5-20 MPa. The medium consistency slurry is prepared in a recirculation loop before passage through the main homogenizing valve which is followed by a plug-flow reactor and a quench system. The process concept derived from our continuous unit is depicted in Figure 1 where steam recovery is illustrated. Steam consumptions of the order of about $1.0\text{ kg steam/kg m.f. wood}$ are possible using steam recompression technologies and medium consistencies (15% wt solids). The molasses-rich hemicelluloses can reach 10% sugar content with the above mentioned steam consumption.

THE REACTION ORDINATE APPROACH

The important question arising from processing lignocellulosics via steam/aqueous systems is how yields of treated fiber as well as yields and characteristics of the extractable constitutive polymers can be related to the severity of the treatment.

In a previous paper (Overend and Chornet, 1987)⁶ we have shown how temperature and time are combined into a single parameter, the reaction ordinate (defined as the 'P' factor), to follow and monitor the changes of the constitutive polymers. Examples of the applicability of the reaction ordinate concept were presented in our previous article using available yield data from well documented steam explosion experiments.

The use of a reaction ordinate is well established in the pulp and paper industry. Its basis is that conventional kinetics cannot account for the complex heterogeneous structural lignocellulosic system. Thus Brasch and Free (1965)³⁷ proposed the use of a reaction parameter, P_t , which combines temperature and time as:

$$P_t = \exp[(T_r - T_b) / 14.75]$$

where T_r is reaction temperature (in $^\circ\text{C}$) and T_b is a base temperature, taken as a reference. In our case, $T_b = 100^\circ\text{C}$.

For an isothermal process, the product of P_t and t , the time of reaction, is the 'P' factor. Since the temperature of the substrate may be subjected to a non-isothermal heat-up period for short reaction times, the generalized reaction ordinate is more appropriately expressed as:

$$R_o = \int_0^t \exp[(T_r - T_b) / 14.75] \cdot dt$$

The 14.75 term can be related to a conventional energy of activation by assuming that the overall pretreatment process is hydrolytic and that conversion [i.e., 1-(total pulp yield)] follows first order kinetics.

The reaction ordinate concept has proven quite useful in mapping the extent of prehydrolysis. In fact, we now consider, based on quantitative evidence (Overend and Chornet, 1989)³⁸, that steaming pretreatment and aqueous prehydrolysis, as for instance in Kraft pulping, are variations of a more general hydrolytic process and can be monitored through the use of the reaction ordinate R_o .

Extension of the reaction ordinate analysis to organosolvent treatments has also proven useful in trying to represent the structural and chemical changes taking place during pretreatment, and even liquefaction (i.e. solubilization) of the constitutive polymers, via a single severity parameter (Chornet and Overend, 1988³⁹; Chornet and Overend, 1989⁴⁰).

The application of the reaction ordinate to steaming processes has been recently discussed based on a case study on Populus tremuloides (Heitz et al., 1988)⁴¹. It was found that the recovery of the constitutive polymers was a rather continuous and smooth function of the severity parameter.

New information on pretreatment of Stipa tenacissima gathered in our slurry unit by Belkacemi, (1989)⁴², is depicted in Figure 2 as a function of reaction ordinate. The ordinate represents the % pentosans in the washed treated fiber relative to the initial pentosan content of the untreated material. The data suggest that with no acid added the cleavage of pentosans begins at $\log R_o = 2$ and it becomes rather extensive beyond $\log R_o = 3$. Figure 2 also shows that the presence of acid (expressed as % wt acid on fiber) has a marked effect on pentosan content in the treated fiber, facilitating the hydrolytic reactions which, as previously indicated, are the predominant reaction of pretreatment processes.

Figure 3 shows the recovered pentosans present in the filtrate derived from hot water washing (~ 70-80°C) and filtration of the treated fiber. It is worth noting that the presence of acid decreases the amount of recovered pentosans and shifts the maximum yield to lower severities.

The fact that the recovery of pentosans is slightly less than the pentosans lost in the fiber (Figure 2) suggests that the presence of acid probably catalyses the homogeneous degradation of pentosans into furfural.

The regular changes observed in the data and their hydrolytic nature, as suggested by their dependence on acid concentration, points out that the treatment severity, i.e. the reaction ordinate, should also incorporate an acid function which will directly affect the hydrolytic mechanisms.

Another set of information on steam/aqueous treatments is provided by our data on Populus deltoides (Bouchard et al., 1989¹³; Bouchard and Chornet, 1988⁴³). Figure 4 shows the variation of the constitutive polymers as a function of severity (no acid added). It is clear that the main effect of the treatment is the solubilization of the hemicelluloses and of a small fraction of the lignin.

The treated and water-washed fiber is literally a ligno-cellulose mixture. Further extraction of the lignin using aqueous caustic solutions has proven to yield consistently higher values than using an alcohol (i.e. ethanol) washing in the 60-90°C range. Figure 5 shows the alkali extracted lignin as a function of treatment severity. The recovered lignin is thus a strong function of the reaction ordinate and, at a severity of $\log R_0 = 3.8$, where a maximum recovery of pentosan is achieved, about 80% of the lignin can be extracted and precipitated.

The lignin precipitation from the alkali solution is made with acid addition. This is a delicate step. The shape and size of the precipitated lignin spheres is a strong function of operating conditions. Operational rules are difficult to detail since the chemical characteristics of the lignin and the presence of minor quantities of sugars influence the nucleation and settling kinetics. Figure 6 shows a typical lignin recovered from Populus species after controlled acid precipitation. It is worth noting the nearly perfect spherical morphology of the lignin "balls".

The cellulose present in the hardwoods does not solubilize until the severity has increased to values beyond $\log R_0 > 5$. This means that it can be quantitatively recovered after lignin extraction at $\log R_0$ around 3.8. During the course of the steam/aqueous treatment the cellulose undergoes depolymerization. Figure 7 shows the degree of polymerization of Populus tremuloides subjected to a steaming treatment in the STAKE II digester.

The cellulose begins to depolymerize at $\log R_0 = 3$ and very rapidly decreases its degree of polymerization. The control of this depolymerization, via alkali addition, may be essential for pulping applications.

The accessibility of cellulose to enzymes can also be "monitored" as a function of $\log R_0$. Figure 8 shows the digestibility of treated Populus tremuloides as a function of the reaction ordinate. The data suggests that the treatment severity has a marked influence on accessibility. Furthermore, it indicates that the maximum digestibility is reached at or around the optimum R_0 value for pentosans recovery. No significant gain is achieved, in total cellulose digestibility, by operating at higher severities, although the enzymatic rates may vary with severity.

The fiber characteristics of the treated lignocellulosics at a severity of 3.8 are depicted in Figure 9. Destructuring and disaggregation result in some fiber damage as shown in the microphotographs. The fibrillar structure of the fibers is apparent from the greatest enlargement.

PROCESS CONSIDERATIONS

Heat and mass transfer limitations are characteristic of steaming processes. When chips are used, experiments conducted at Forintek (1985)⁴⁴ have led to the conclusion that reaction times of less than 2 min. at high temperatures will result in significant undercooking of chip centres. When small particles, shavings and sawdust are used together, as in the case of residual material, the heat penetration inside the lignocellulosics bed is indeed a limiting factor when using batch reactors. There is, however, no significant constraint with continuous digestors which mix and turn the solid material inside the reactor regardless of particle dimensions. To overcome heat penetration limitations in batch reactors we have found that moisture content of the feedstock must be increased to about 50% by weight. Addition of steam results in rapid and rather uniform heat transfer through the moist material.

In liquid-phase systems, where typical particle dimensions are 0.5-1.0 mm, heat up times are very short since they are dependent on the high thermal conductivity of water. Also, we have found that penetration of acid/base homogeneous catalyst can be well accomplished by either long periods of swelling or the use of homogenizing valves which, as previously indicated, facilitate inner solvation of the particles. The addition of acid/base homogeneous catalysts to chips used in steaming processes requires a prior impregnation step.

The energy, i.e. steam, required to heat wood chips to the reaction temperature is a direct function of the initial moisture content of the material. For a reaction temperature of 220°C the steam required per kg of dry wood ranges from 0.3 at 9% moisture content to 0.7 at 50% moisture content. The aqueous slurry technique at 15% consistency requires about 1 kg of live steam per kg of dry wood. Although these amounts could be lowered by using steam recompression techniques, the recompressed steam is also needed to raise, by evaporation, the dissolved solids content of the hemicelluloses-rich molasses.

The presence of oxygen, from air either present in the pores of the lignocellulosics or entrained inside the reactor, is deleterious to the treatment since it induces significant oxidation reactions at high temperatures. Presteaming of chips is a valuable alternative practiced by the pulp and paper industry. The use of oxygen scavengers in aqueous-slurry systems is also an option to consider in order to decrease the extent of unwanted oxidations which impart dark colour to the fibers and give rise to acidic functionalities in cellulose.

The presence of water is essential to the hydrolytic processes. A properly conducted experiment requires control of the "free water" during the treatment. It is essential that the material is well wetted since only by the presence of water can hydrolysis and H-bonding changes be induced as previously discussed.

When deciding on specific process conditions, the key step is to define the temperature-time sequence for a given operation. The overall data base on hardwoods provides the following guidelines:

- the recovery of the pentosans is optimized, for hardwoods, at $\log_{10}R_0 \approx 3.8-4.0$. A yield of 65-75% of the initial pentosans present in the wood is achieved at this optimum, depending on the biomass type;
- the recovery of lignin via alkali (0.4% wt) extraction can reach 75-80% of the initial lignin present in wood at $\log_{10}R_0 \approx 3.8$. Increased severities result in higher lignin yields;
- cellulose is entirely recovered at $\log_{10}R_0 \approx 3.8$ although its degree of polymerization begins to decrease significantly at $\log_{10}R_0 > 3.0$ as shown in Figure 7.

For stalks (corn stover, bagasse, etc.) and straw, the same patterns seem to hold but slightly different severities are needed to reach similar recoveries.

Softwoods are more difficult to treat than hardwoods and the available data suggest that catalyst addition is required to achieve a significant fractionation.

CONCLUSIONS

Steam explosion and aqueous slurry treatments are essentially thermo-mechano-chemical processes in which the predominant reaction is thermal hydrolysis with water being a reactant. In steam explosion systems mechanical effects are due to sudden decompression which forces flash evaporation of the internal water present in pores, inducing massive destructuring and disaggregation. In aqueous systems mechanical effects can be induced via rapid passage through orifices or homogeni-

zing valves. The mechanism causing mechanical effects is not clear but it could be due to cavitation effects caused by vapor microbubbles inside the liquid slurry.

Steam- and aqueous-phase pretreatments can effect a separation of the feedstock into two fractions: an aqueous extract rich in hemicellulose derivatives along with some water-soluble lignin, and a pulp composed of cellulose and an easily extracted lignin.

The reaction ordinate used to monitor and follow the recovery of pentosans, extractable lignin and residual cellulose has proven to be an adequate marker of the severity of the pretreatment process. It permits the correlation of data obtained in different reactors provided the temperature-time sequence is known. Furthermore, key structural parameters such as degree of polymerization of cellulose and enzymatic digestibility can be adequately represented as a function of the reaction ordinate.

The fractions derived from steam- and aqueous-phase pretreatments can be further used via novel and conventional upgrading routes. New product development schemes can now be pursued since the technology to produce the basic primary fractions is commercial either in batch or continuous processes. This opens the way for a progressively increased utilization of biomass via chemical and biotechnological approaches.

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U of S - F aqueous steam system

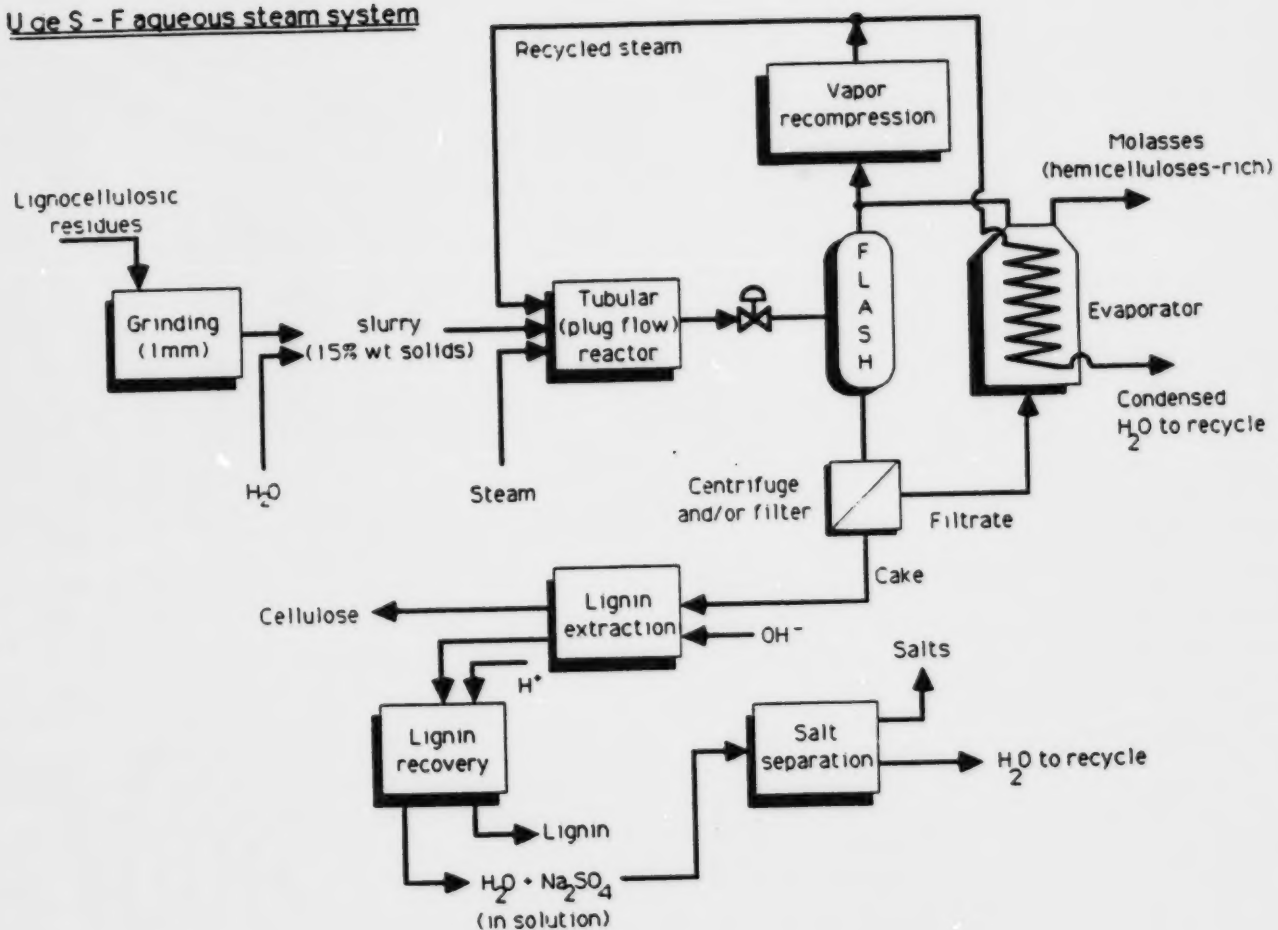


Figure 1. Process diagram for a typical aqueous/steam system

STIPA TENACISSIMA

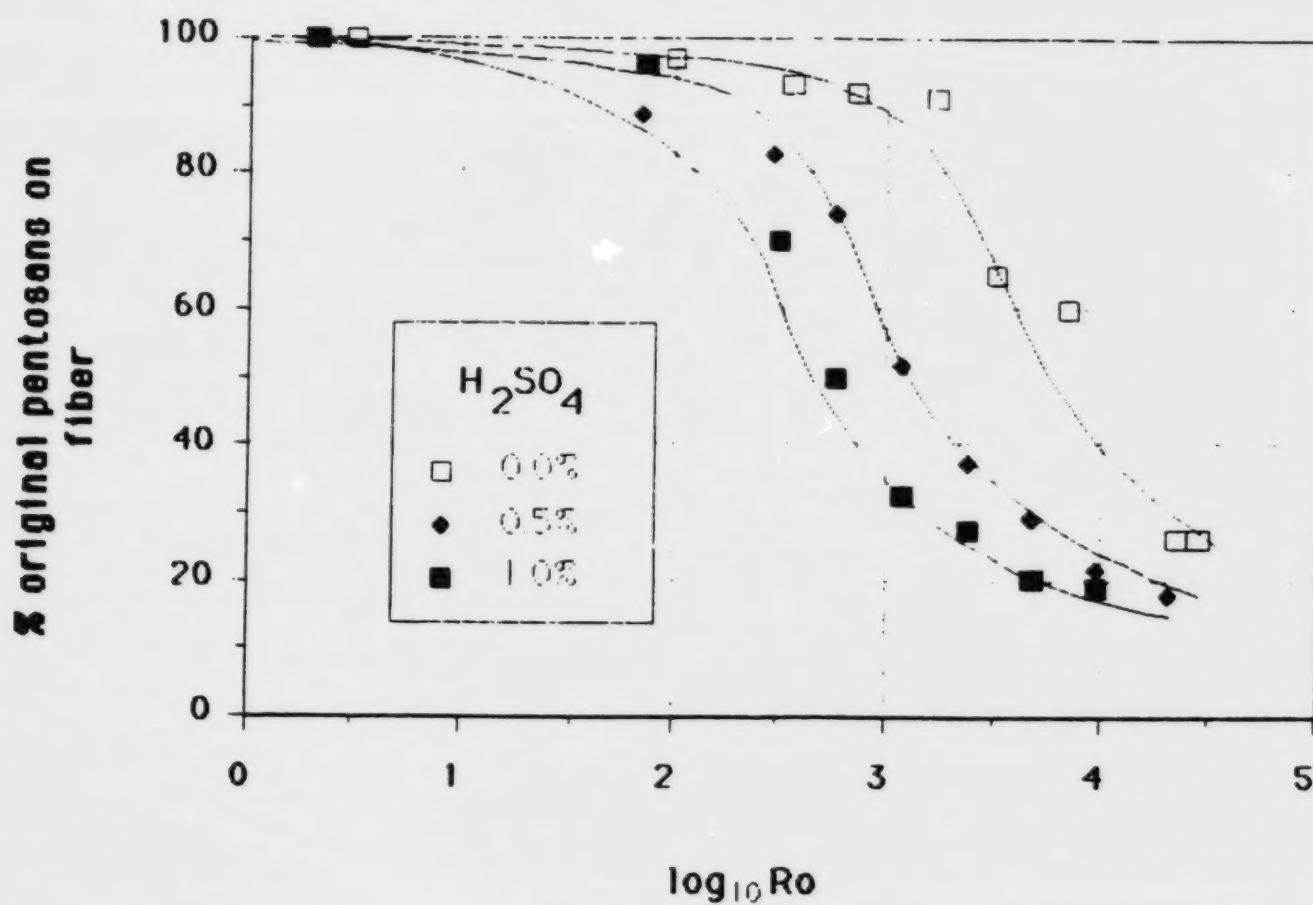


Figure 2. Pentosans present in treated fiber as a function of severity (Belkacemi⁴²). R_o is expressed in min.

STIPA TENACISSIMA

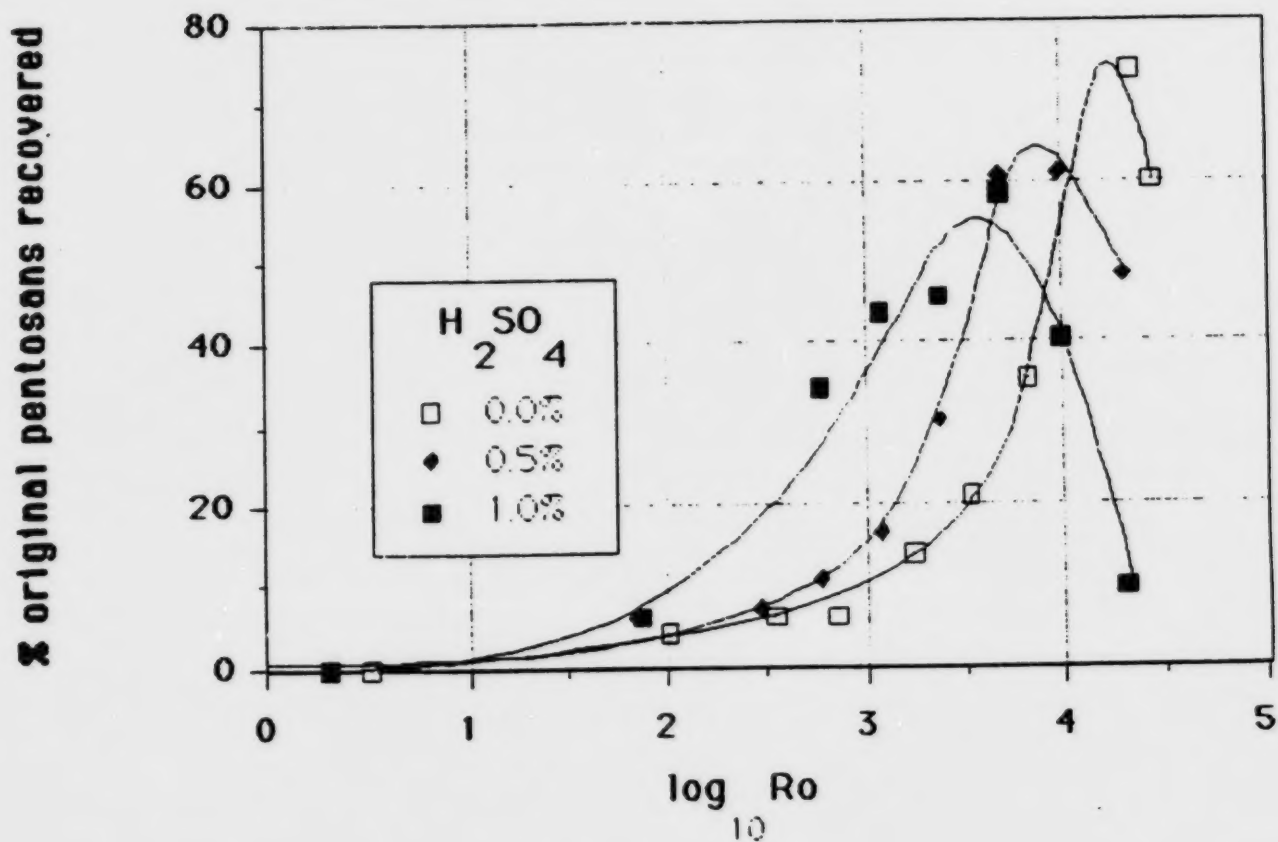


Figure 3.

Recovered pentosans in aqueous filtrate resulting from hot water extraction of the treated fiber (Belkacemi⁴²). R_0 is expressed in min.

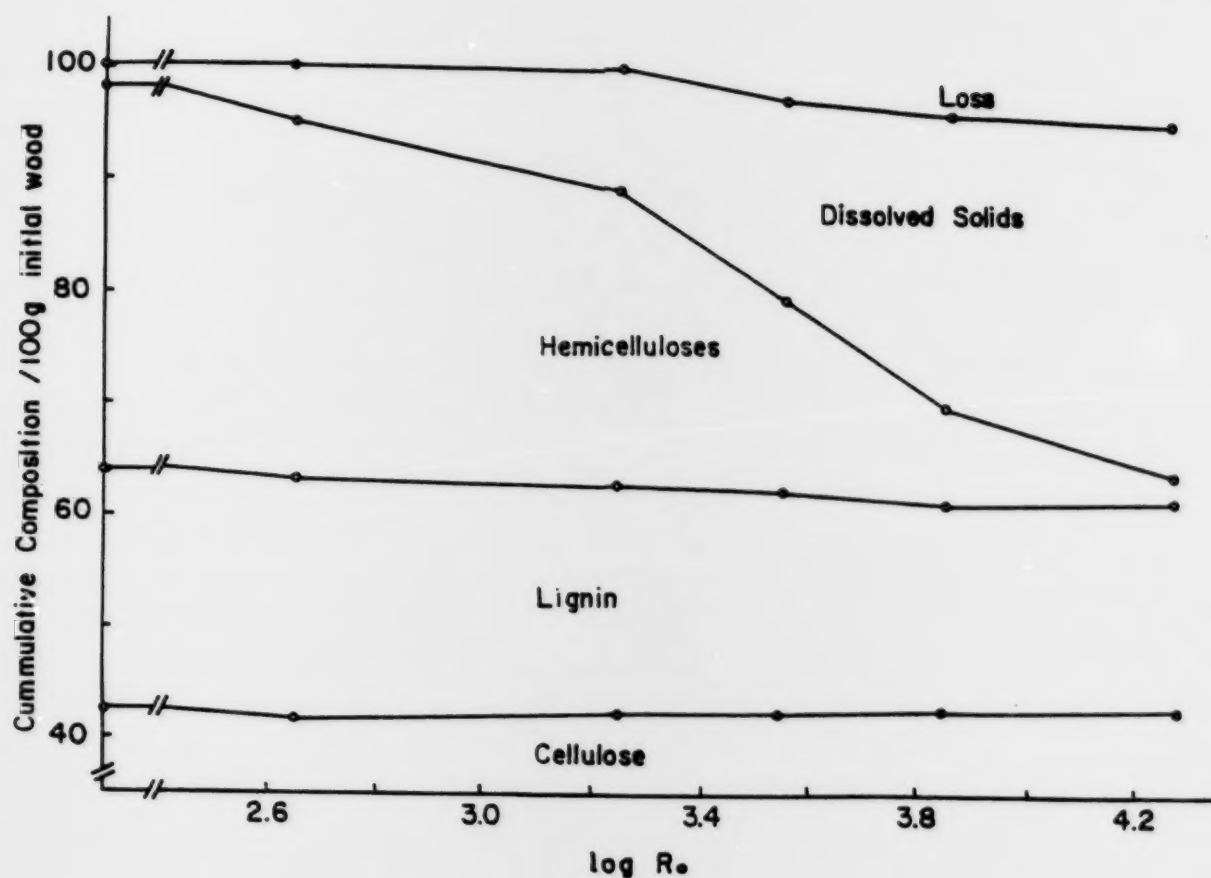


Figure 4. Course of the constitutive polymers during aqueous/steam pretreatment of *Populus deltoides* (Bouchard et al.¹³). The ordinate expresses the cumulative composition in g/100 g of initial dry wood. The units of R_0 are min.

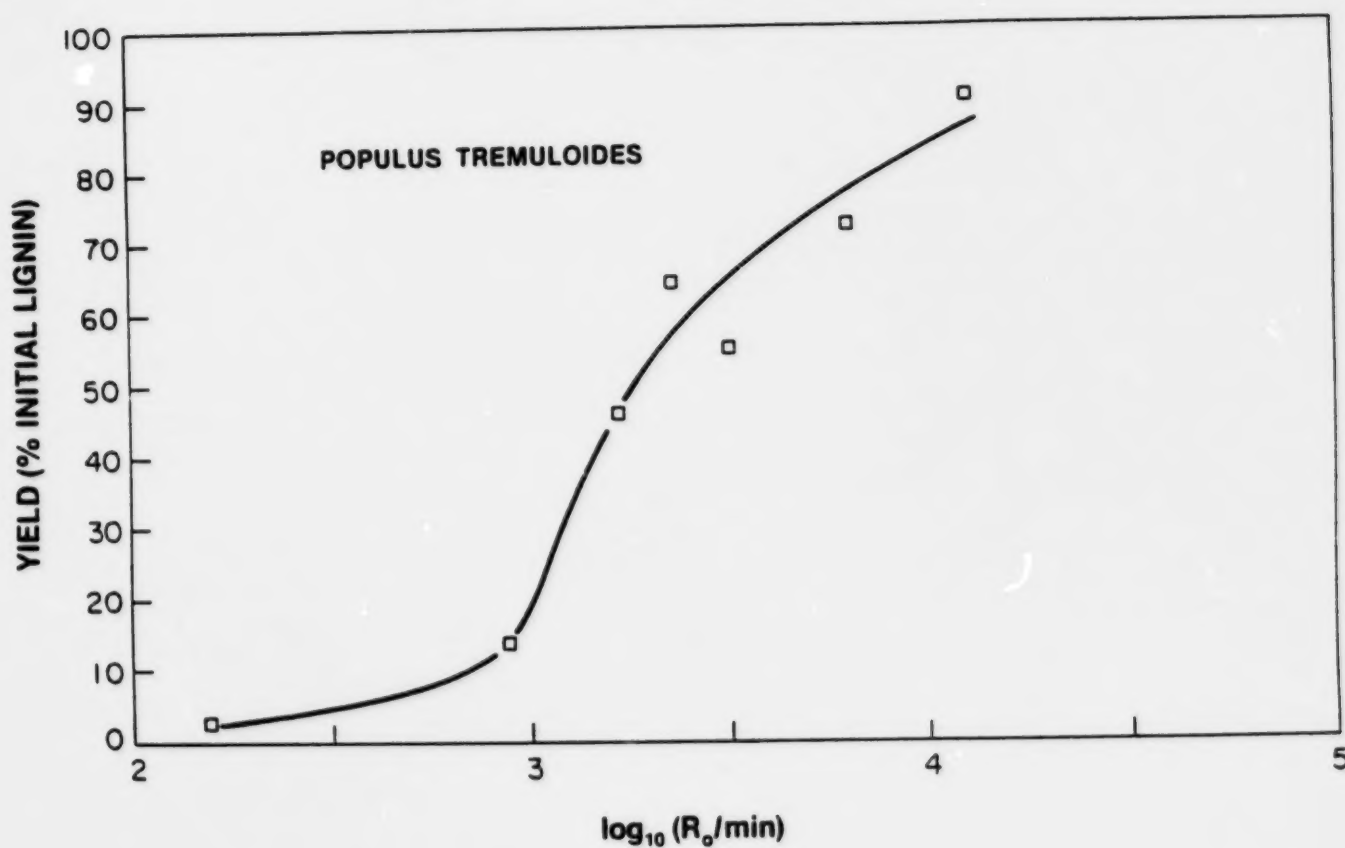


Figure 5. Lignin recovery as a function of treatment severity (Heitz et al.⁴¹). R_0 is expressed in min.

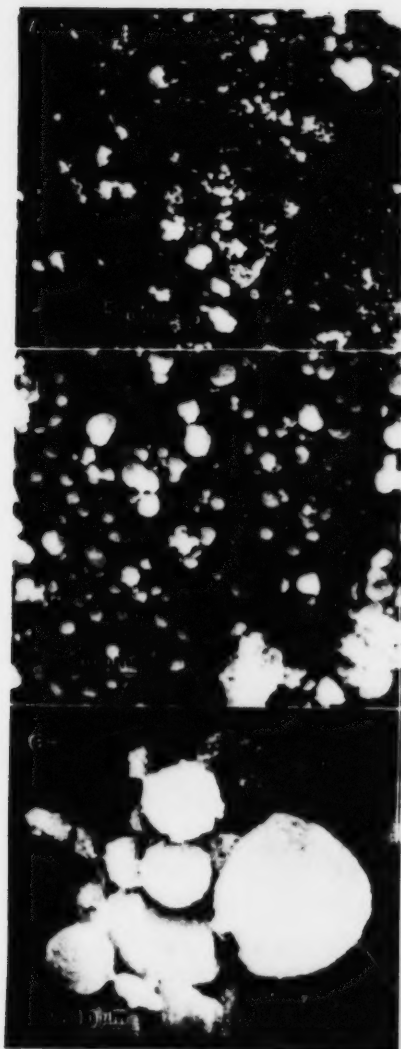


Figure 6. Lignin spheres acid-precipitated from alkali solutions following aqueous-steam treatment

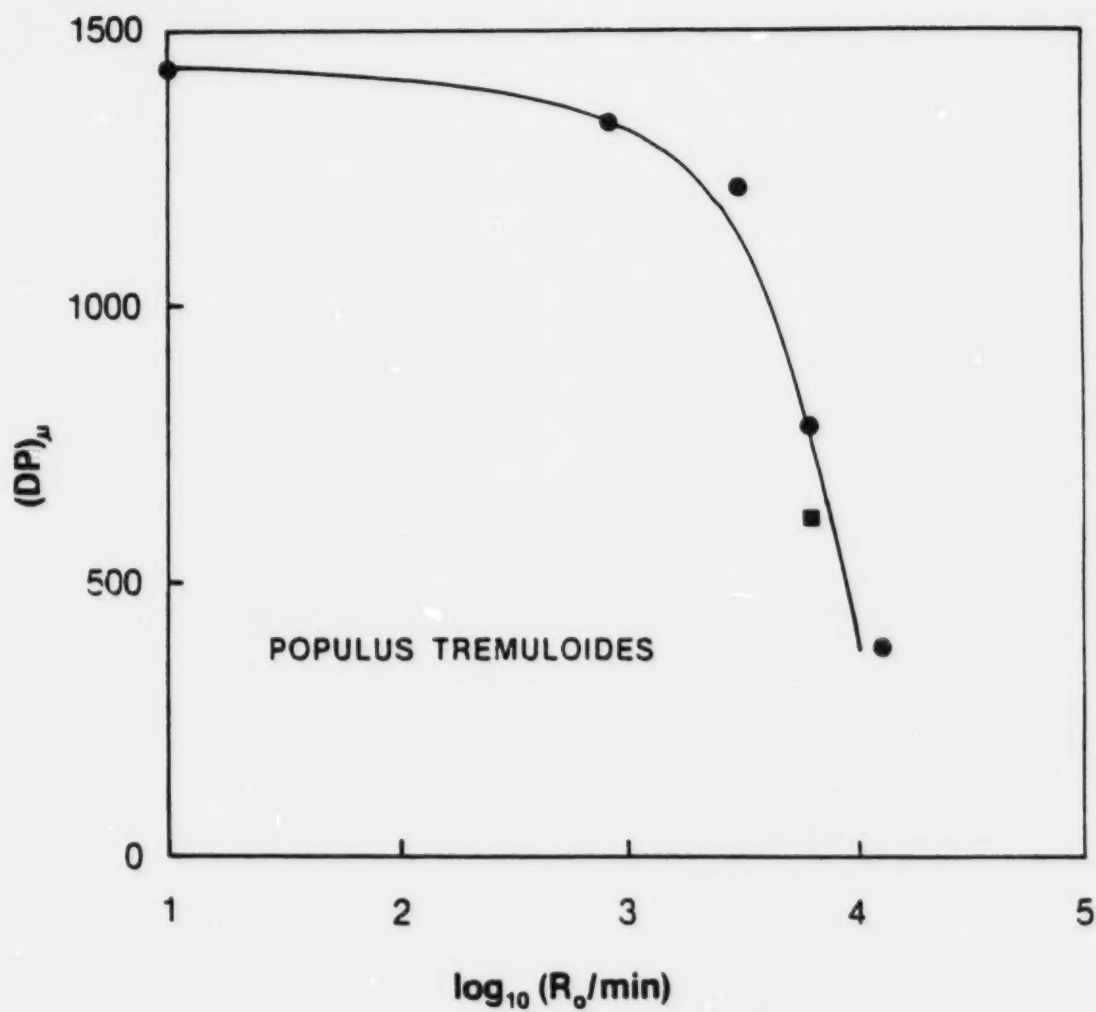


Figure 7. Degree of polymerization of cellulose as a function of severity (Heitz et al.⁴¹). Units of R_0 are min.

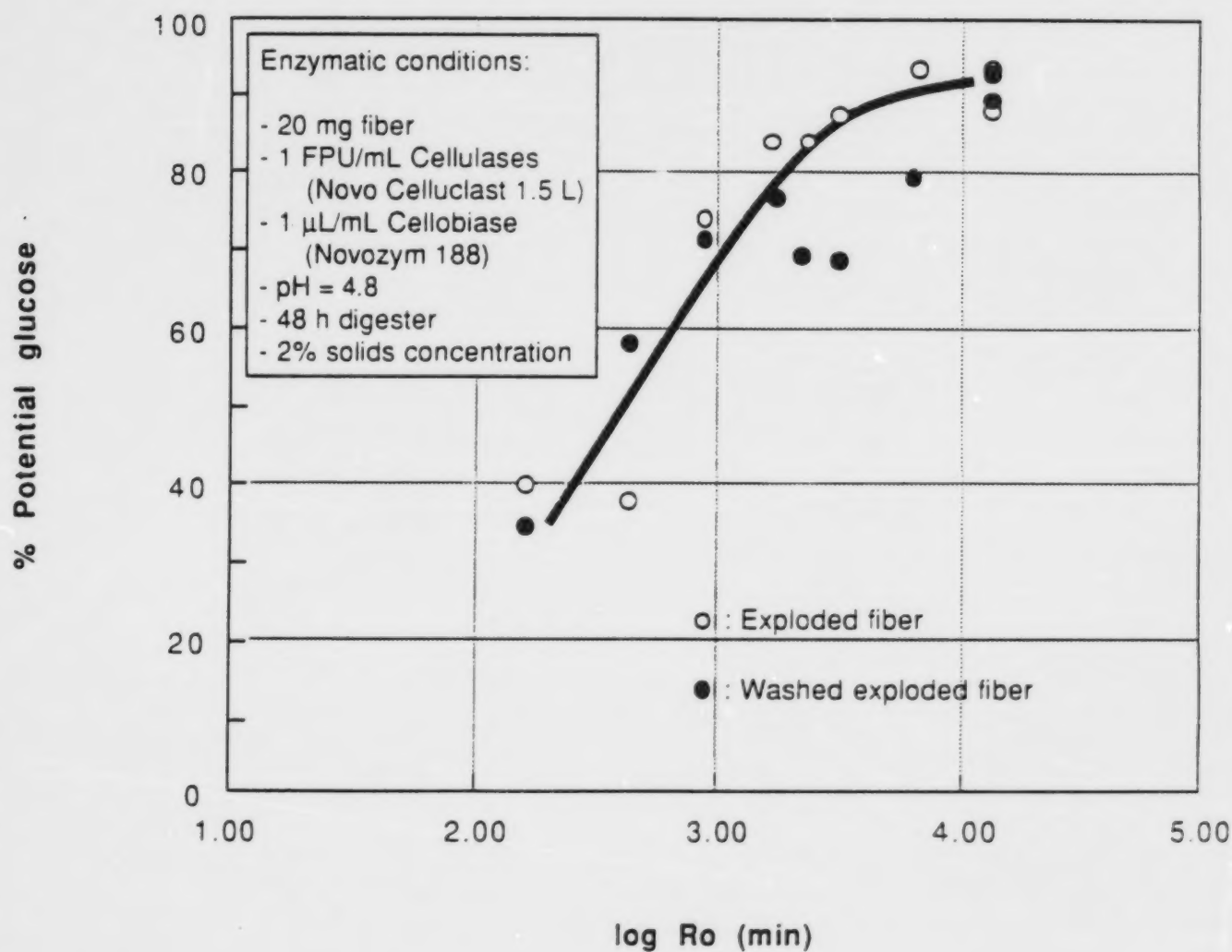


Figure 8. Enzymatic digestibility of steam-exploded *Populus tremuloides* as a function of the reaction ordinate (Heitz et al.⁴¹).

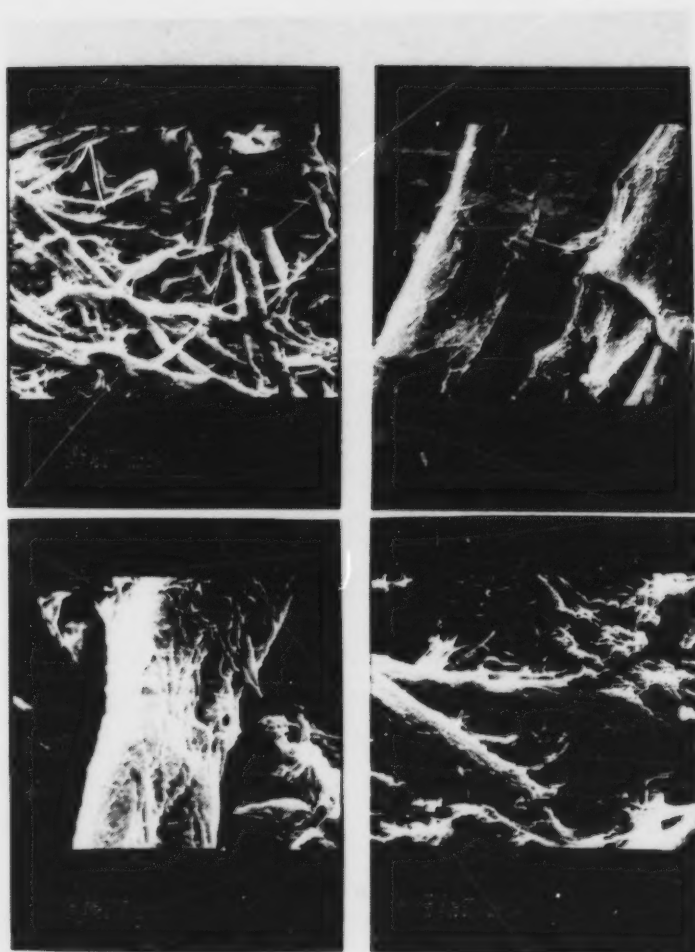


Figure 9. Scanning electron micrographs of pretreated Populus deltoides at a severity of $\log_{10}R_0 = 3.8$

SECTION B: FRACTIONATION OF POPULUS TREMULOIDES AT THE
PILOT PLANT SCALE: OPTIMIZATION OF PRE-
TREATMENT CONDITIONS VIA STEAM EXPLOSION
USING THE STAKE II TECHNOLOGY

by

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ABSTRACT

The optimization of the fractionation of a prototype hardwood, Populus tremuloides, was conducted in a 4 tonnes/h pilot plant STAKE II unit located in Sherbrooke, Québec. The aim of the optimization was to find operational zones which maximize the recoveries of the constitutive fractions, namely: hemicelluloses (pentosans), lignin and cellulose. To accomplish this, our group has used a phenomenological approach based on the definition of a severity parameter $R_0 = t \cdot \exp [(T-100)/14.75]$ which combines time (t, min.) and temperature (T, °C) to express the severity of a given pretreatment.

Performance curves, using the R_0 parameter, have been experimentally developed. They indicate that the maximum recovery of pentosans is 65% of the initial pentosans present in the untreated fiber at $\log_{10}R_0 = 3.8$. Under these conditions, lignin recovery by caustic extraction is around 80% of total lignin. The cellulose is entirely recovered at this severity and needs to be bleached to achieve its natural coloration. At severities both greater and lesser than $\log_{10}R_0 = 3.8$ the pentosans recovery decreases.

The cellulose derived from the steam fractionation process is rapidly depolymerized at severities beyond $\log_{10}R_0 = 3.2$. Its enzymatic digestibility is close to theoretical in the ranges of severities comprised between 3.2 and 4.1. The latter is the highest severity explored in our work.

The results obtained clearly suggest that steam explosion processes are fundamentally hydrolytic in nature and they represent the extension into high severities of existing thermomechanical treatments.



INTRODUCTION

Previous studies on fractionation of lignocellulosics have led to a detailed understanding of the behavior of the constitutive polymers during steam/aqueous treatments, a generic term which covers steam-explosion techniques. Thus in a series of papers, it has been established (Overend and Chornet, 1987) that steam/aqueous treatments are essentially hydrolytic in nature and the yields of the constitutive fractions can be well represented by a simple severity parameter, analogous to the P-factor used to model prehydrolysis during pulping operations. In a more recent paper, it has been shown that steam-aqueous treatments are indeed thermo-mechano-chemical approaches and can be considered as an extension of the lower severity treatments used in the pulp and paper operations and in the fiberboard industries (Chornet and Overend, 1989).

The literature on steam explosion can be grouped into four categories corresponding to four distinct applications:

- (i) as a pretreatment process for increased accessibility of the carbohydrates to enzymatic digestion;
- (ii) as a defibration process to prepare a substrate for the fiberboard industries;
- (iii) as a destructuring and disaggregation process to facilitate separation of lignin, hemicelluloses and cellulose;
- (iv) as a destructuring process for high yield pulp production.

This section concerns the third category of processes which aims at the maximum recovery of the constitutive polymeric families for specific end uses. The hemicellulose liquors rich in pentoses can readily become the raw material for a variety of chemicals among which furfural and xylitol are direct and prominent examples. A xylitol production plant, using the STAKE feeder-digester technology, has operated since 1988 in Kokta (Finland) using the hemicellulose liquor derived from steam explosion of hardwoods. The lignin recovered after extraction is the subject of increasing interest due to recent major advances in the understanding of the relationship of structure/functionality/performance in various polymeric applications, as pioneered by the work of Glasser and co-workers (Glasser et al., 1983; Chum et al., 1985; Robert and Bardet, 1985). The lignin fraction has also been considered as a source of oxyaromatic compounds via thermal or catalytic depolymerization (Goheen, 1971; Lin, 1983). The cellulose fraction can be recovered entirely until very high treatment severities are reached (see Overend and Chornet, 1987 and references therein). The glucosidic bonds are, however, progressively hydrolyzed with increasing treatment severities, and the trend of the degree of polymerization is towards the level-off degree (LODP) found in acid hydrolysis experiments.

The above discussion makes the point that the steam-aqueous treatment conditions (i.e. temperature and time) to be chosen for a process will depend upon the yields and physico-chemical characteristics of the desired fractions. Moreover, the addition of acid or basic catalysts can profoundly change the product characteristics. Thus, the presence of SO_2 , which leads to the formation of in situ acid, enhances the enzymatic digestibility of the carbohydrate fractions in coniferous materials (Wayman et al., 1986), whereas the presence of NaOH facilitates de-structuring and defibration of hardwoods with minor changes in the cellulose, the net result being the possibility of production of high yield pulps having excellent paper-making characteristics (Kokta, 1989).

Although abundant information on steam explosion applications is readily available in the literature, few data have been reported on the fractionation of lignocellulosics based on experimentation at the commercial or demonstration plant levels. Furthermore, most of the available data are derived from discontinuous or batch "guns" in which heat transfer rates are limiting, resulting in the significant undercooking of chip centers for reaction times of less than 2 min at high severities (Lachenal and Monzie, 1985; Forintek, 1985; Overend and Chornet, 1987). We thus felt that a systematic study using a continuous feeder-digester combination, i.e. the STAKE II system, would add valuable information to the existing data base on steam explosion and would also show how the severity parameter approach can be used advantageously to map the experimental conditions in the range of interest for the fractionation of the lignocellulosic material.

A thorough study on the fractionation of wood via steam explosion using a continuous feeder-digester STAKE reactor has been reported by Muzzy et al. (1983). The work consisted of treating chipped tulip poplar (*Liriodendron tulipifera*) at two levels of saturated steam pressure (2.51 MPa and 2.17 MPa corresponding to treatment temperatures of 224.2 and 216.7°C, respectively). The digester residence time was varied between 3 and 7 min at reaction temperature. The corresponding severity using the reaction ordinate $\log_{10}R_0$ (Overend and Chornet, 1987) ranged between 3.9 and 4.5. This places the study in the medium severity range where decomposition of pentose sugars leads to the formation of furfural and degradation products which copolymerize with lignin resulting in higher amounts of NaOH -extractable material (i.e. "pseudolignin") than the initial Klason lignin content of the original wood. Further evidence for the formation of pseudolignin is the increased amounts of acetic acid and furfural found in the steam condensate as a function of severity as shown in Figure 1. The results of Muzzy et al. (1983) also point to a recovery of glucose which is essentially equal to the theoretical although the glucose present in the treated fiber, i.e. a close measure of the recovered cellulose, decreases with severity $\log R_0 \geq 4.1$.

The goals of our investigation were three-fold: (a) to optimize the fractionation of a prototype hardwood, Populus tremuloides, by determining how the yields of pentosans, lignin and cellulose vary as a function of the reaction ordinate, $R_0 = t \exp [(T-100)/14.75]$; (b) to explore the low severity range, $\log R_0 < 4.0$, as a means of limiting the extent of recondensation reactions; (c) to determine the average degree of polymerization of the cellulose present in the treated fiber. We felt that this could be a key indicator for possible uses of the fiber in specific pulping applications.

EXPERIMENTAL

(a) Wood material

Ten tonnes of Populus tremuloides from the Eastern Townships (Quebec) were debarked and chipped across the grain using conventional equipment common to the pulp and paper industry. The shavings had as average dimensions: 2.0 cm x 2.0 cm x 0.2 mm.

The composition of the chipped material, which was determined using the standard methods (ASTMD-1103-60 for α -cellulose; ASTMD-1787 for pentosans; and ASTMD-1106 for ash), was (in % wt m.a.f. wood): ethanol-toluene extractives, 3.6%; pentosans, 19.0%; cellulose, 51.6%; Klason lignin, 20.6%; other hemicellulosic material, obtained by difference, 5.2%. The ash content was 0.4% wt m.f. wood.

The chipped material was used fresh, at moisture contents comprised between 45 and 55% of the total weight of the chips. The experiments were conducted during a two-week period which accounted for the differences in the observed moisture range.

(b) Pilot plant

The steam explosion facility used for this work is located in Sherbrooke, Québec. The installation of the pilot plant was begun in 1985, and the peripheral equipment and data acquisition system were operational at the end of 1986.

The key technological component of the pilot plant is the STAKE II feeder-digester having a nominal biomass treatment capacity of 4 tonnes/h. A diagram of the pilot plant facility is shown in Figure 2a. The location of pressure and temperature sensors is indicated in Figure 2b. The raw material is conveyed to a storage bin from where it is withdrawn through an auger which moves the material towards a chute into the coaxial feeder. The latter moves and compresses the material forming a dense plug which enters the digester by exerting a pressure against a choke cone. A hydraulically-operated automatic system adjusts the back pressure of the choke cone against the plug.

Once the material is at the digester inlet it is moved towards the discharge end by a system of augers while exposed to saturated steam for a prescribed period of time, which can be adjusted by varying the speed of the augers. The augers discharge the material through a Kamyr blow valve (3.2 cm internal diameter at the throat). The opening frequency of the blow valve can be adjusted with a timer or via a feedback loop which is based on the torque generated by the accumulation of the treated material onto the last transfer auger. The frequency of the discharge was varied from 1 to 6 sec between openings of the blow valve. The latter remains open for 0.3 sec during which a mass of the material is discharged through a 15 cm pipe into a receiving bin. Due to the high steam pressure inside the digester, the velocity through the blow valve approaches the velocity of sound and a small detonation accompanies each blow valve opening.

The transported wet treated material is disengaged from the steam by a tangential cyclone located just at the entrance of the 15.2 m³ receiving bin. This volume is sufficient to dampen adequately the detonation or "steam explosion". The wet treated material falls onto the floor of the receiving bin from where it is continuously conveyed to the final discharge point. The exit steam is sampled through an aspiration-condensation sampling train operating at 1-1.5 l/min of condensate.

The steam is produced by a 200 h.p. Clayton flash boiler having a maximum thermal steam output of 7.0 GJ/h. Injection of the steam is made through three inlet ports located adjacent to the choke cone area. A vortex shedding type flowmeter (YEWFLOW) is attached to the steam line to measure steam consumption.

The data acquisition system is a Hewlett-Packard Model 3497A. Through five connectors we are able to record 20 analog-input (T, P, flows) channels, 16 numerical-input (pulses, events, etc.) channels and 16 programmable relays. The HP3497A unit is connected to a HP9000 computer which, through appropriate interfaces, is linked to the operator's terminals. Sampling of input data (T, P and flow rates) was chosen to be carried out at 10 sec intervals.

(c) Experimental plan

In order to optimize the fractionation of Populus tremuloides we designed an experimental plan based on the use of the reaction ordinate R_0 previously defined as a key indicator of the severity of the treatment. The implicit assumption is that the destructuring, disaggregation and depolymerization profiles of the constitutive wood polymers can be represented as a function of the reaction ordinate even if the exact mechanisms are unknown for the complex macromolecular system under study. By scanning the reaction ordinate from a region of low severity, i.e. $\log_{10}R_0 \approx 2$, where the destructuring begins, to a region of high severity, i.e. $\log_{10}R_0 \geq 4$, where depolymerization and recondensa-

tion reactions are important, the experimenter can rapidly (i.e. with relatively few experimental points) obtain the conditions at which optimum separation and recovery of the constitutive polymers takes place. The following grid of experiments was carried out:

Treatment temperature (°C)	Treatment time (min)	$\log_{10}R_0$ (R_0 in min)
180	2	2.66
180	0.7	2.20
180	4	2.96
200	2	3.25
210	2	3.54
220	2	3.83
220	0.7	3.37
220	4	4.13
230	2	4.13

(d) Treatment and separation methodology

The procedures used for treatment and separation are shown in Figure 3. The steam-exploded material was sampled as it was produced, and 1 kg lots were sealed in plastic bags and frozen until the analyses were performed.

The optimization of the separation sequence involved three crucial steps: (i) the water extraction of the treated fiber to recover the soluble sugars; (ii) the alkali delignification of the cellulosic residue; (iii) the precipitation and recovery of the lignin.

The water extraction step was studied at 5-6% fiber consistency and as a function of temperature. It was found that a sequence of two washings at 70°C for 0.5 h gave as good results as any higher temperature up to 100°C.

The delignification step required optimization of the suspension consistency, the temperature, the pH and the time. It was found that the optimum laboratory conditions were 5% wt fiber consistencies, 100°C, pH = 13 (NaOH added) and 30 min as delignification time. The sus-

pension consistency was varied up to 10% wt of fiber, the extraction yield being then slightly below that at 5% wt fiber consistency.

Conditions for the precipitation of the lignin were found to be optimum at 80°C, pH = 1.5-2.0 (H₂SO₄ added) and 10 min as contact time. The filtrate resulting from the delignification step contained small amounts of soluble hemicellulosic material which were not recovered nor quantified in our study.

Quantification of the recovered pentosans, cellulose and lignin were made using the standard methods already mentioned in the materials section. Two other indicators were monitored in the cellulose and lignin fractions: (a) the degree of polymerization of cellulose was measured via the determination of the intrinsic viscosity of the cellulosic material dissolved in cupri-ethylenediamine (Browning, 1967); (b) the carbon content of the lignin was determined via a Perkin-Elmer, model 240C, analyzer.

(e) Enzymatic digestibility of treated fiber

The methodology described by Capek et al. (1987) was followed. It consisted of preparing an aqueous suspension of the fiber at 2% wt fiber consistency in a total of 1 ml 0.05 N sodium citrate buffer, pH 4.8, containing 0.005% sodium azide, 1.0 FPU/ml of cellulase (Celluclast) and 1 µl/ml of cellobiase (Novozym 188). Incubations were performed in capped test tubes in duplicate. Samples were incubated while shaking (90 cycles/min) at 50°C for a maximum of 48 hours. At different times, samples were removed, centrifuged at 3000 • g for 5 min, and 25 µl of the supernatant were analyzed for glucose and total reducing sugars.

Glucose analysis was performed using a Beckman Astra 4 instrument based on the measurement of the oxygen consumed by the glucose oxidase reaction. Reducing sugars were determined by the method of Halliwell and Halliwell (1984) using a glucose standard, so that the results are presented as glucose.

RESULTS AND DISCUSSION

The operational stability of the STAKE II reactor during a run is illustrated in Figures 4 and 5 where the temperature inside the digester (thermocouple T2) and the pressure of operation (gauge P1) are shown as a function of the operating time as recorded by the data acquisition system. The intermittent nature of the operation both at the inlet and outlet ends of the reactor did not affect the thermal and pressure stability of the system. The oscillations shown in the bottom parts of both Figures 4 and 5 are due to the cycling frequency of the discharge blow down valve.

The feeding rate to the reactor is also quite constant for a given run as shown in Figure 6 where the number of revolutions of the transfer auger

(charging bin to coaxial feeder) is recorded during the same time interval as the one considered in Figures 4 and 5. Note that the biomass feed rate is directly proportional to the slope of the straight line shown in Figure 6. In our experimental runs the STAKE II feeder-digester operated at feed rates between 1.5 and 2.5 tonnes/h of green chips.

Samples of the treated fiber were subjected to exhaustive H₂O washings at conditions shown in Figure 3. The water-soluble material was thus separated from the insoluble solids. In Figure 7 we have plotted the extent of solubilization (g of water solubles/100 g of untreated dry wood) as a function of treatment severity. The data shows that significant solubilization requires treatment severities beyond $\log_{10}R_0 = 3$ and that the extent of formation of water-soluble material increases very slowly (i.e. the slope of the curve is essentially zero) at severities beyond 3.75. The important conclusion from the results presented in Figure 7 is that at $\log_{10}R_0 < 3$ the "steam explosion" process may lead to destructuring effects without significant hydrolytic bond rupture, a prerequisite for solubilization. The latter requires higher severities (i.e. $\log_{10}R_0 > 3$) to take place at any significant rate for this hardwood species. The work reported by Schultz et al. (1983, 1984) using mixed hardwood chips, and using a 28.3 L Masonite gun, provided a similar solubilization profile. A general distinction between destructuring and hydrolysis can thus be made around a severity of $\log_{10}R_0 \sim 3$ for hardwoods.

In an effort to understand which chemical constituents were being solubilized during the steam explosion treatment, we have plotted the pentosan content of the treated fiber before and after water extraction in Figure 8. The ordinate in Figure 8 represents the yield of pentosans defined as the ratio of fibre pentosans to the initial pentosans present in the untreated wood. It seems clear from Figure 8 that an increase in treatment severity leads to significant losses of pentosans possibly as furfural (Figure 1) and degradation products. Also, from Figure 8 one can infer that the difference in pentosan yields between the pretreated and H₂O-extracted fiber should correspond to the pentosans found in the H₂O extract. The latter are shown in Figure 9 which also shows that there is a maximum pentosan recovery at around $\log_{10}R_0 = 3.8$ for this hardwood species. This maximum recovery is about 65% of the original pentosans. These recovered pentosans were a mixture of oligomers and monomers. A thorough analysis of these water-soluble fractions has been well documented by Barnet (1984) for similar hardwood species.

The H₂O-extracted fiber was subsequently delignified using the procedure shown in Figure 3. The yields of "lignin" expressed as percentage of the Klason lignin present in wood are shown in Figure 10. The trend is towards increased lignin recovery with increasing severities. Analyses of the C, H and O contents of these lignins clearly indicated that the alkali-extracted material had a similar composition regardless of treatment severity and that the composition was also comparable to that of original Klason lignin. Thus we were confident that at the severities

used we did not induce condensation reactions between lignin and carbohydrate derivatives and we could consequently recover pure fractions of lignin via alkali-extraction followed by acid precipitation. The degree of polymerization and the methoxyl content of these lignins was not determined.

A significant point is that at the maximum pentosans recovery (i.e. $\log_{10}R_0 = 3.8$) the lignin yield is about 75% of the original Klason lignin in the untreated wood. Thus the conditions at which there is an optimum recovery of pentosans do not result in a maximum yield of lignin by the extraction procedure shown in our work. A post treatment or an alternate extraction procedure are needed if a higher ($\approx 90\%$) lignin recovery is desired.

The fiber resulting from the alkali delignification is essentially cellulose with the remaining alkali insoluble lignin and hemicelluloses. Under the severity conditions used in our work the yields of cellulose were, in all cases, 100% of the cellulose present in the original wood. Two characteristics of this cellulose were studied: its degree of polymerization and its enzymatic digestibility as a function of treatment severity.

Figure 11 shows the degree of polymerization of the cellulose as a function of severity. The determination was made using the holocellulose derived from the treated water-extracted alkali-delignified samples. It was felt that the contribution of the residual hemicelluloses present in the samples would be a minor fraction of the intrinsic viscosity of the holocellulose-cupriethylenediamine complex from which the degree of polymerization is derived. Thus by measuring the intrinsic viscosity of the holocellulose we are in fact measuring the contribution of the cellulosic component. The results from Figure 11 clearly indicate a rapid depolymerization whose onset is a severity of $\log_{10}R_0 = 3.0$. At severities of $\log_{10}R_0 = 3.8$ the degree of polymerization, DP, is about 600. These observations suggest that if a high yield pulp is desired, the steam-explosion process should be run at conditions which induce destructuring (to facilitate downstream refining) without extensive depolymerization. This translates into using a maximum severity of $\log_{10}R_0 = 3.0$ which is obtained at 191.6°C and 2 min as treatment. Indeed the work of Kokta (1989) has shown that under very similar conditions good qualities of high yield pulps can be obtained. In Kokta's work, the impregnation with Na_2SO_3 and NaOH helped to achieve the essential properties required of the high yield hardwood pulps. The results in Figure 11 also suggest that if a low yield cellulosic pulp is desired, a severity of $\log_{10}R_0 = 3.8$ (218.8°C and 2 min) is suitable for the direct production of a dissolving-like pulp (DP $\approx$ 600).

Figure 12 shows that the enzymatic hydrolysis of the treated (exploded) fiber and the washed exploded fiber, after 48 h digestion using the enzyme combination detailed in the Figure's caption, approaches 90% of the potential glucose of the samples at severities corresponding to

$\log_{10}R_0 = 4.0$. Also, the enzymatic hydrolysis efficiency increases regularly with treatment severity, suggesting that the destructuring and depolymerization effects are essential to increase the enzymatic susceptibility. Complete digestibility of the cellulosic fraction of the treated fibers was not achieved since most likely, a small fraction ($\leq 10\%$) of the cellulose is chemically modified during the process and thus is not recognized by the enzymes. Evidence for these internal matrix modifications during autohydrolysis has been recently presented by Bouchard et al. (1989).

CONCLUSIONS

The present work has confirmed that the fractionation of hardwoods can be carried out at the industrial scale under steam explosion conditions. Significant yields of pentosans, lignin and cellulose can be readily obtained by adjusting the severity of the operation. A convenient treatment severity for the hardwood studied corresponds to a reaction ordinate $\log_{10}R_0 = 3.8$. At this severity a pentosan recovery of 65% was achieved by simple water extraction of the exploded fiber. This recovery level was the maximum found within the range of severities $\log_{10}R_0 = 2.2$ to 4.1. At $\log_{10}R_0 = 3.8$, about 75% of the potential lignin can also be recovered by direct alkali extraction followed by acid precipitation. The residual fiber contains 100% of the original cellulose plus the unextracted hemicelluloses and lignin residues.

The cellulosic residue obtained after delignification shows an enzyme reactivity which follows the treatment severity. Thus the enzymatic hydrolysis yields rise uniformly with severity reaching 90% of the theoretical yields at a severity of $\log_{10}R_0 = 4.0$.

We have noted that using the degree of polymerization of the cellulose as a marker, steam explosion at low severities, i.e. $\log_{10}R_0 \leq 3.0$, does not result in extensive depolymerization of the cellulose, which maintains a DP above 1000 (intrinsic viscosity method). This readily suggests that the steam explosion treatment is, predominantly, a destructuring effect up to this level of severity. When the severity of the treatment is increased beyond $\log_{10}R_0 = 3$ then hydrolytic reactions (i.e. autohydrolysis) take over as the predominant mechanism and the cellulose depolymerizes rapidly. The degree of depolymerization is strongly dependent upon the treatment severity and a DP ≈ 600 is reached at a severity parameter of $\log_{10}R_0 = 3.8$.

The results also show that steam explosion technologies are mature processes. Operation of the industrial scale reactor STAKE II used in this work has led to consistent observations and reproducible data. The stability of the process in terms of temperature, pressure and flow rates has been demonstrated.

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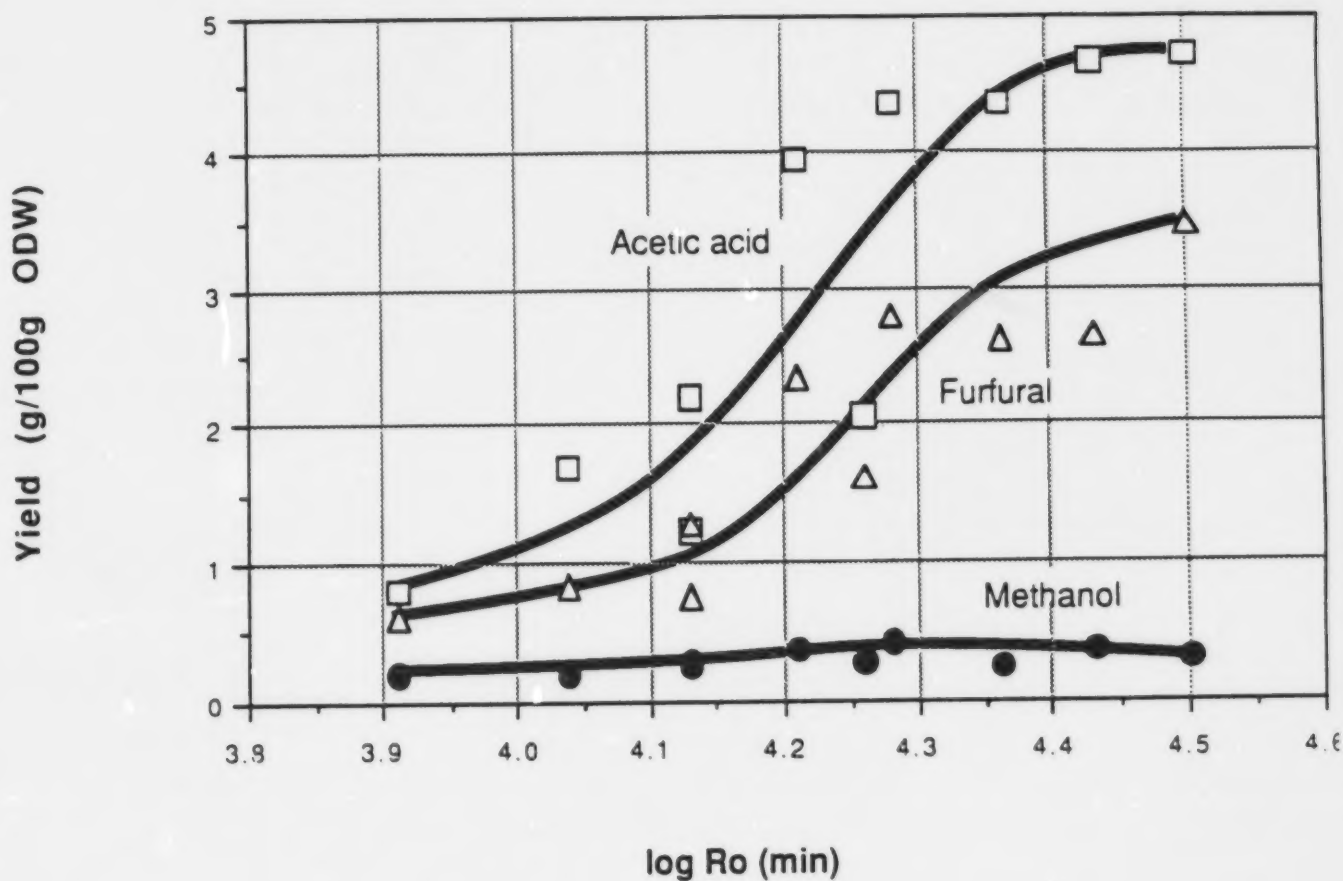


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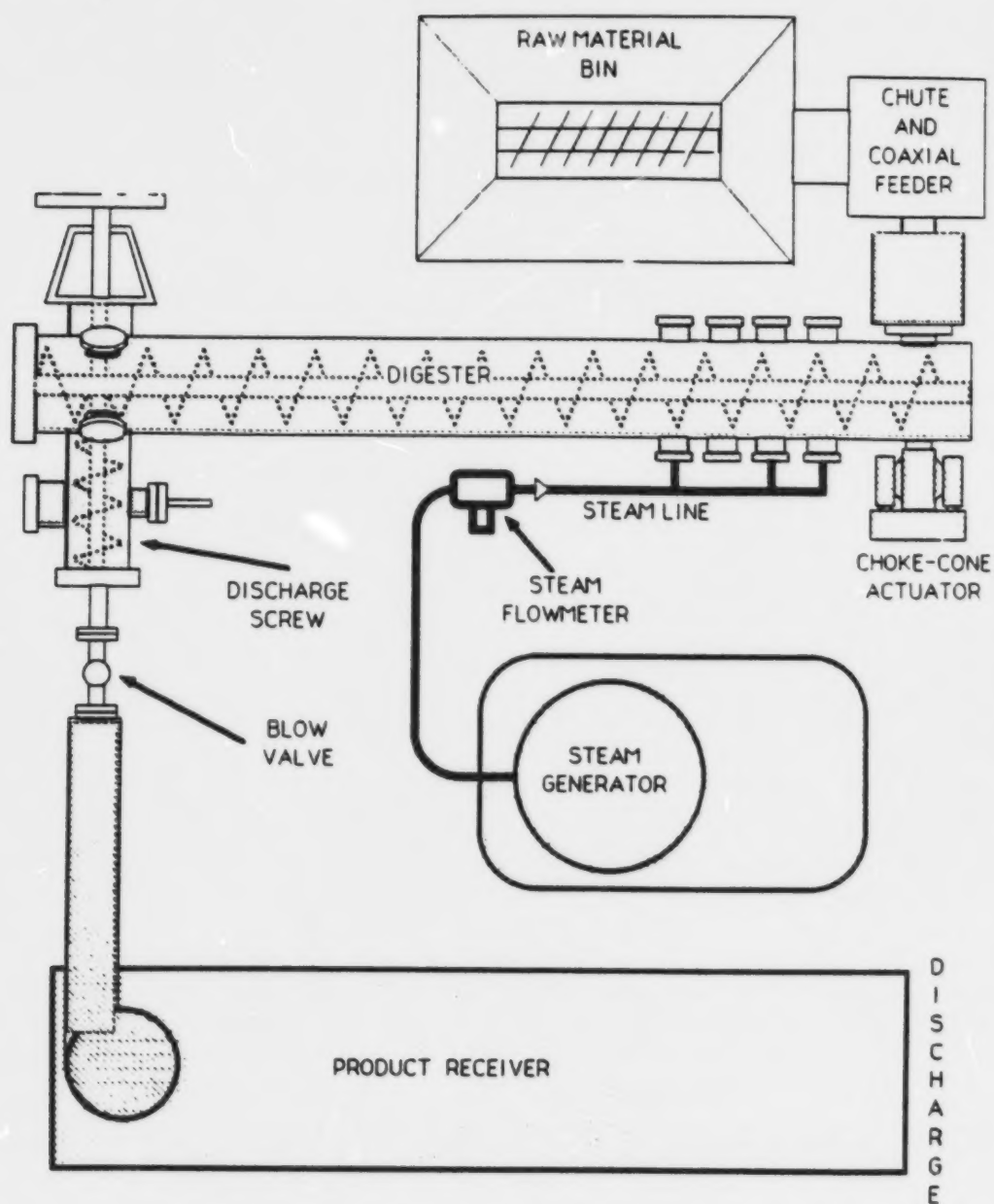


Figure 2a. Schematic diagram of the STAKE II pilot plant facility. The unit, having a maximum treatment capacity of 4 t/h, is located in Sherbrooke, Québec, Canada.

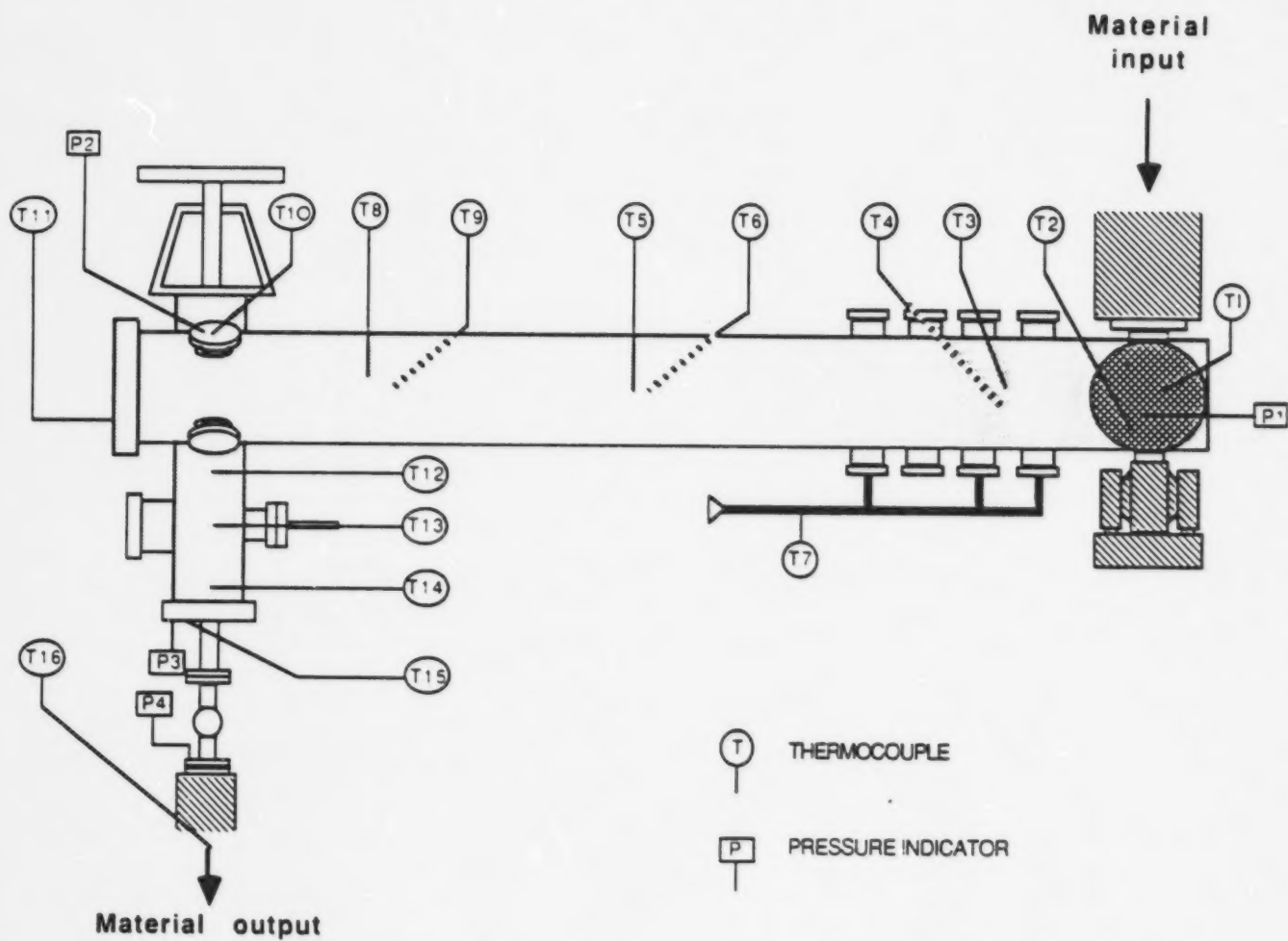


Figure 2b. Temperature and pressure sensors installed in the digester

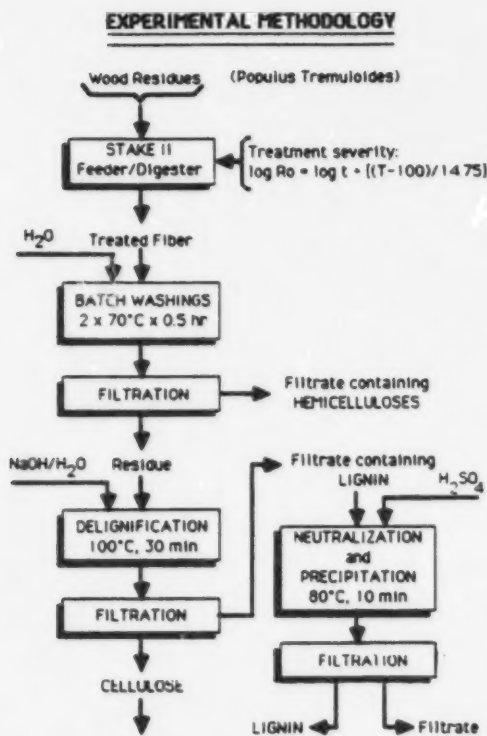


Figure 3. Schematic block diagram showing the analytical protocol used in the experiments

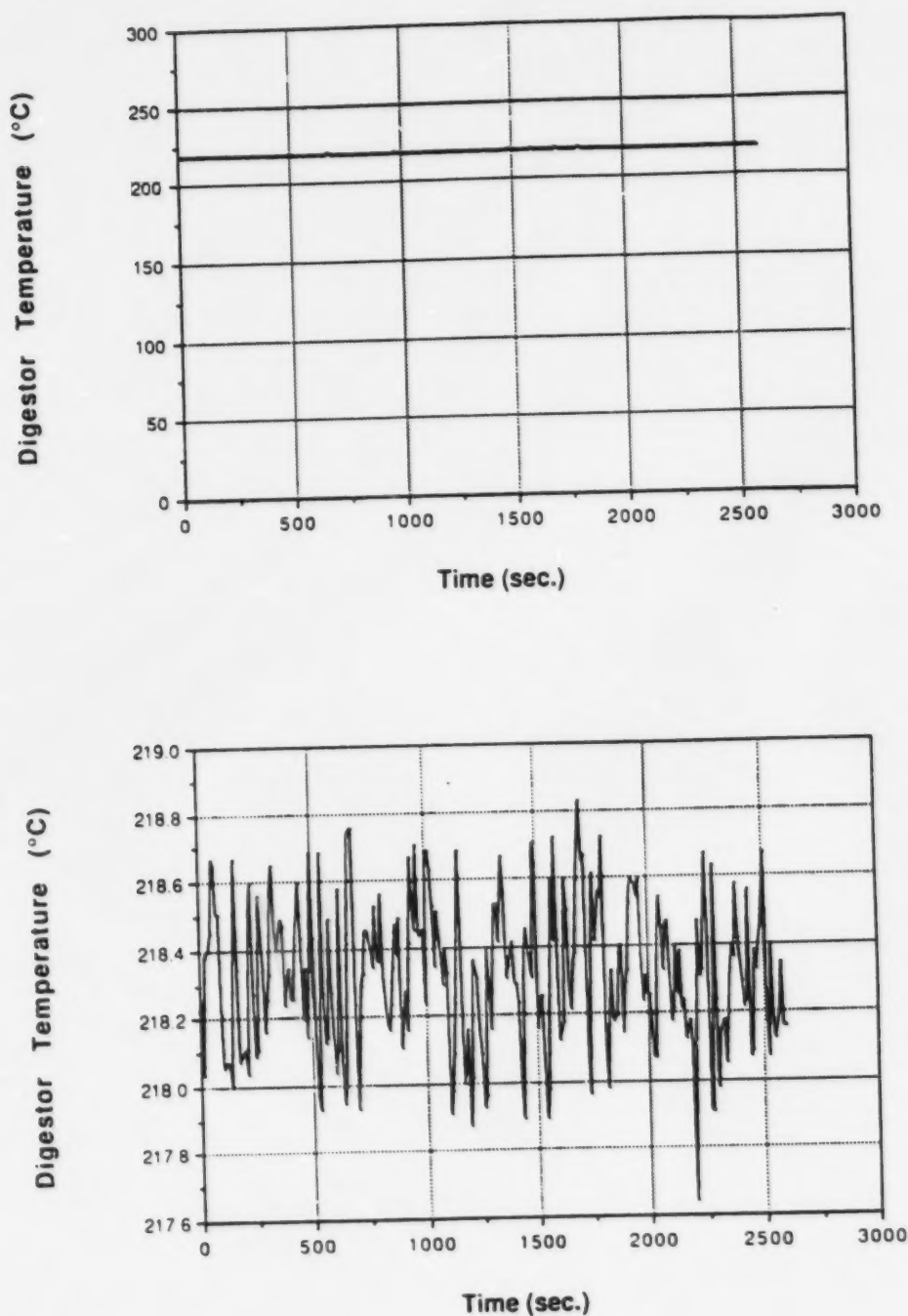


Figure 4. Temperature of the digester as a function of time for a typical run. (Note the small cyclic variations (bottom) which correspond to the frequency of the discharge blow valve opening)

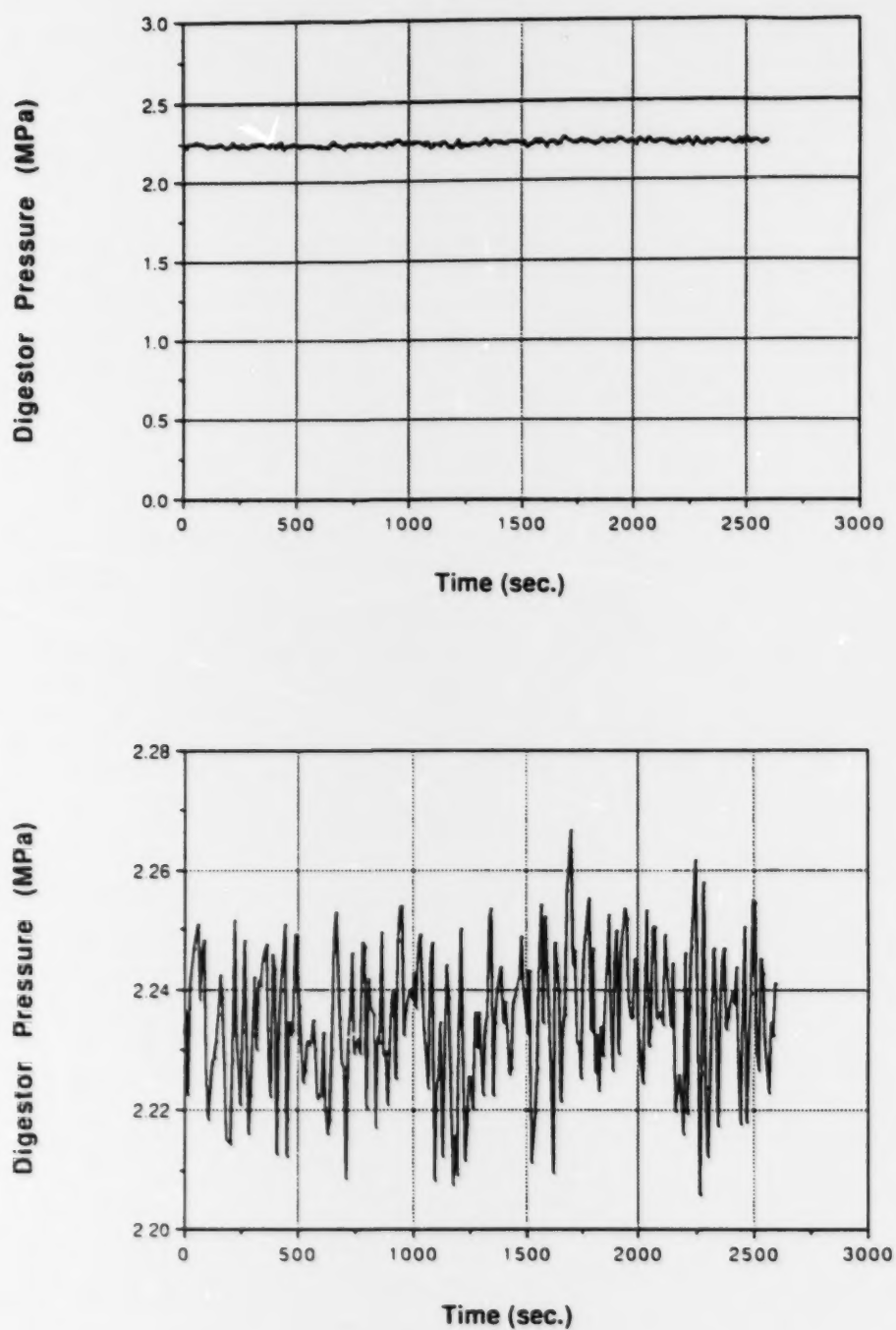


Figure 5. Pressure inside the digester as a function of time for a typical run. (As in the previous Figure 4 note the small cyclic variations (bottom) which correspond to the frequency of the discharge blow valve opening)

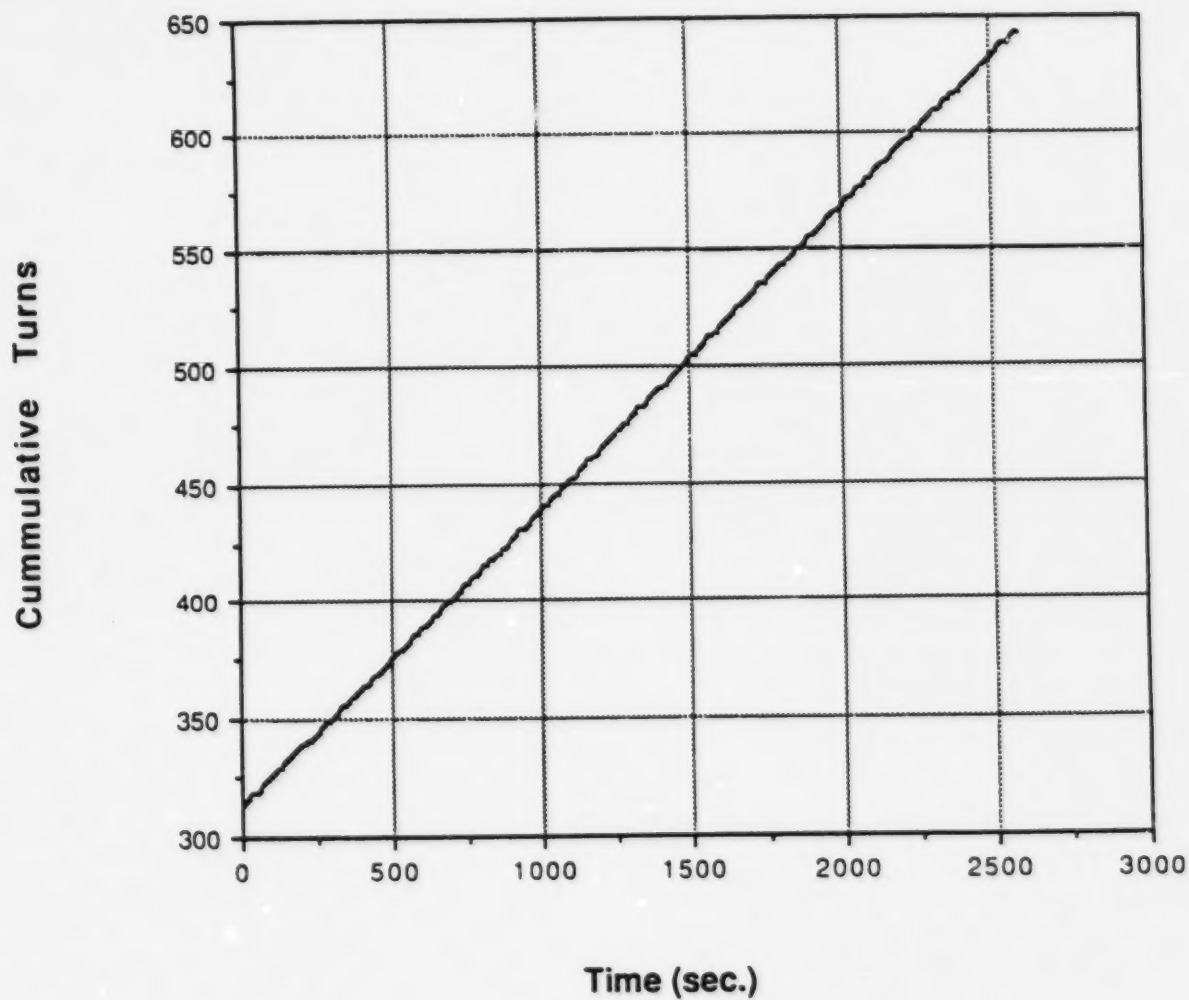


Figure 6. Recording showing the stability of the feeding auger

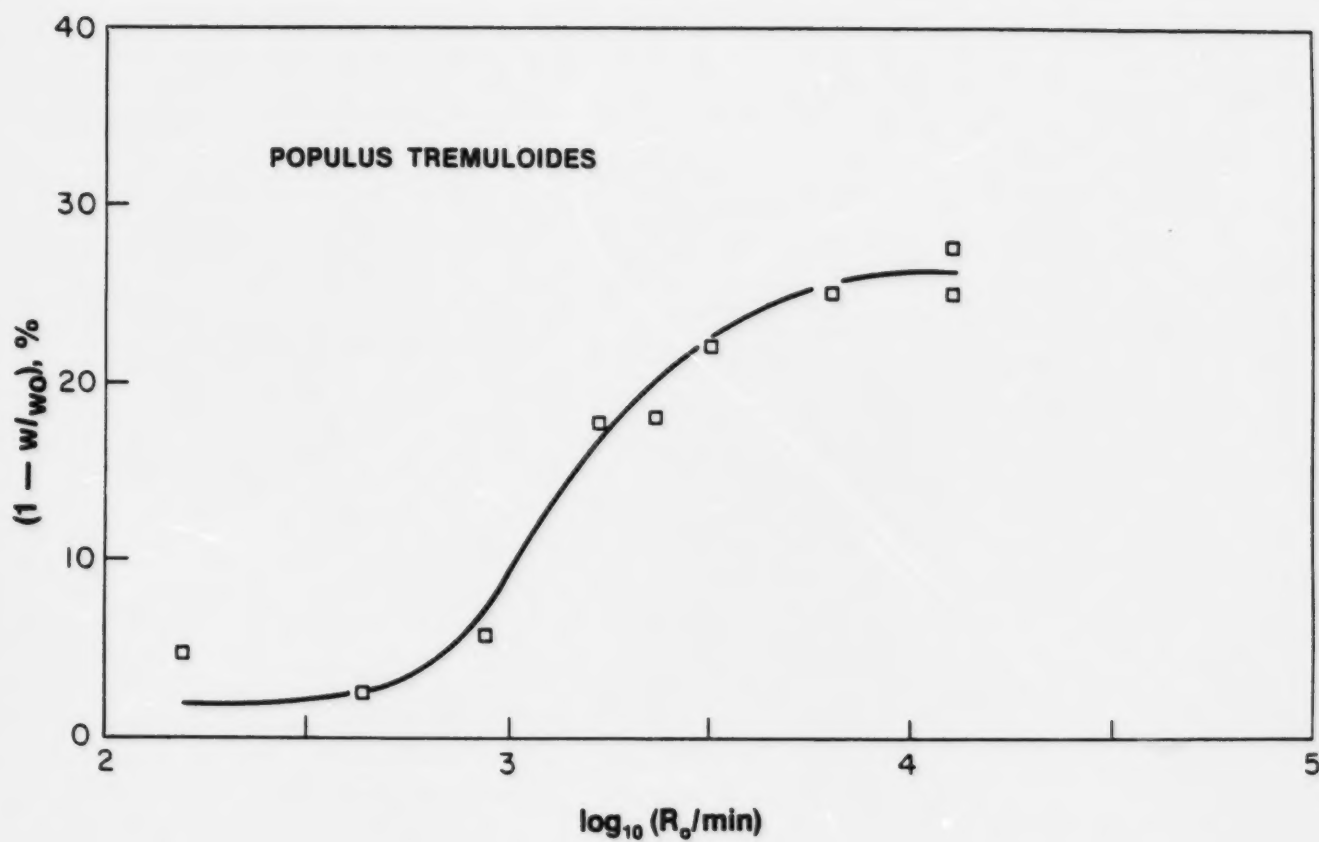


Figure 7. Extent of solubilization (conversion to water-soluble material) as a function of treatment severity. Definitions: w = weight of recovered dry solids; w_0 = weight of input wood

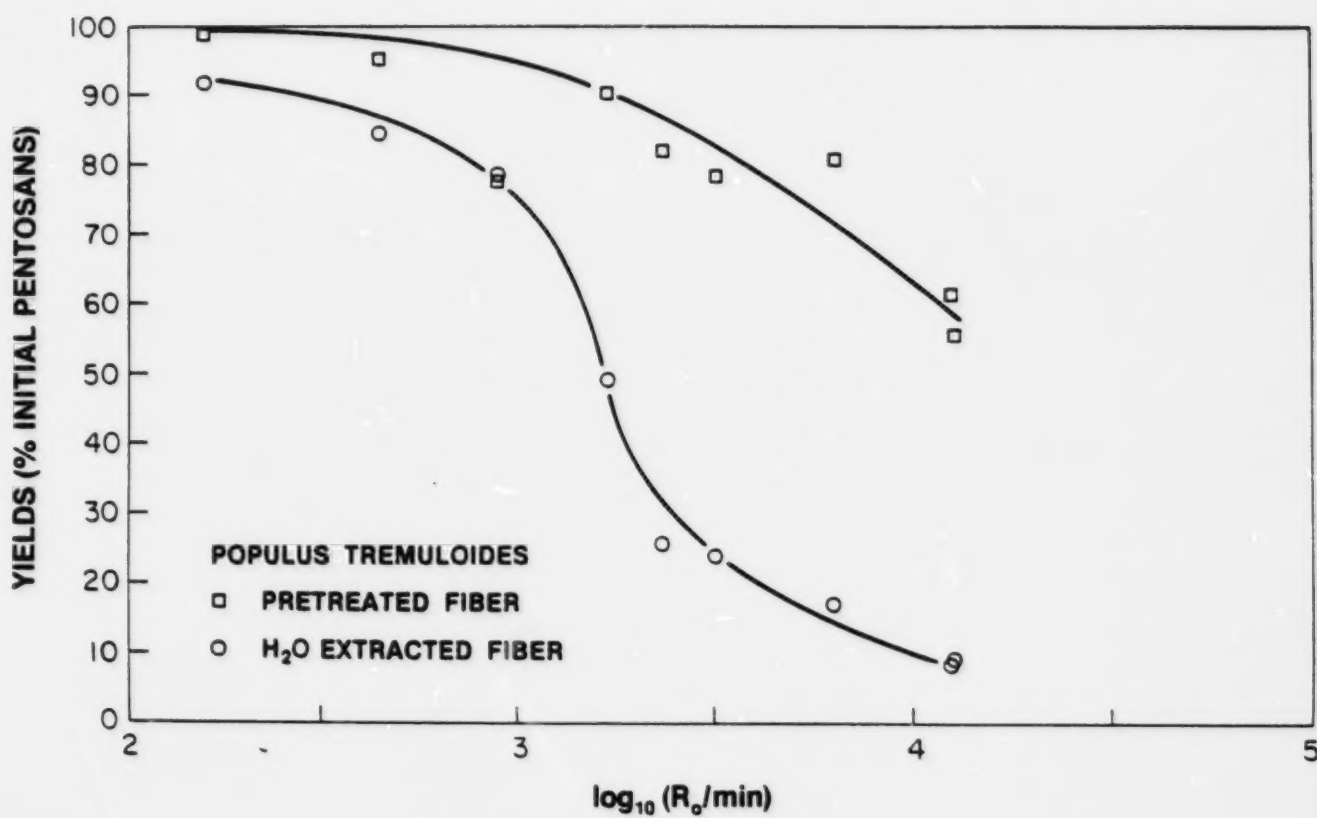


Figure 8. Pentosans found in the exploded fiber before and after water extraction. The ordinate units are the ratio of pentosans measured divided by the pentosans present in the untreated original wood

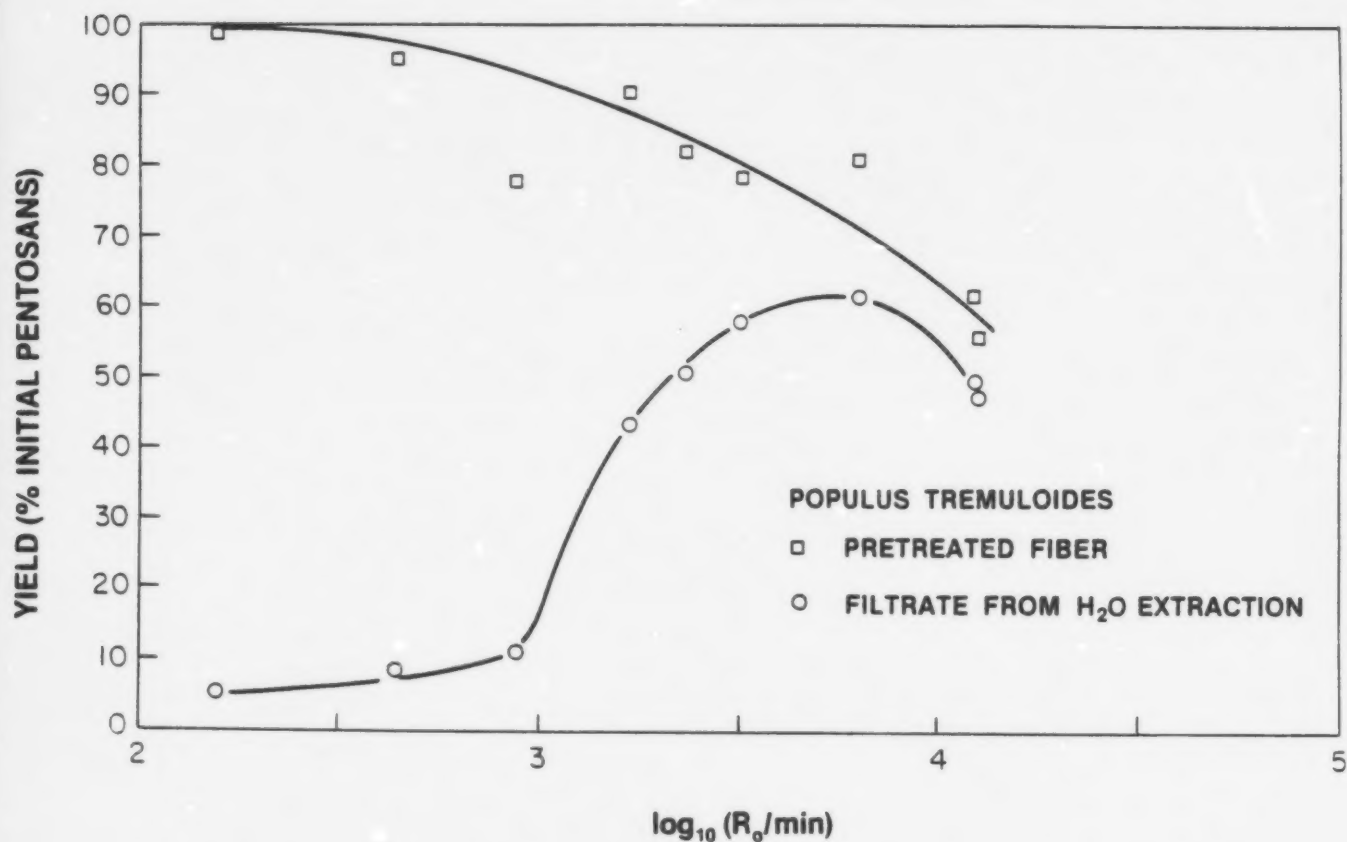


Figure 9. Pentosans recovered in the exploded fiber before water extraction (top points) and in the filtrate following water extraction of the exploded fiber (bottom points). The ordinate units are the ratio of pentosans measured, divided by the pentosans present in the untreated original wood

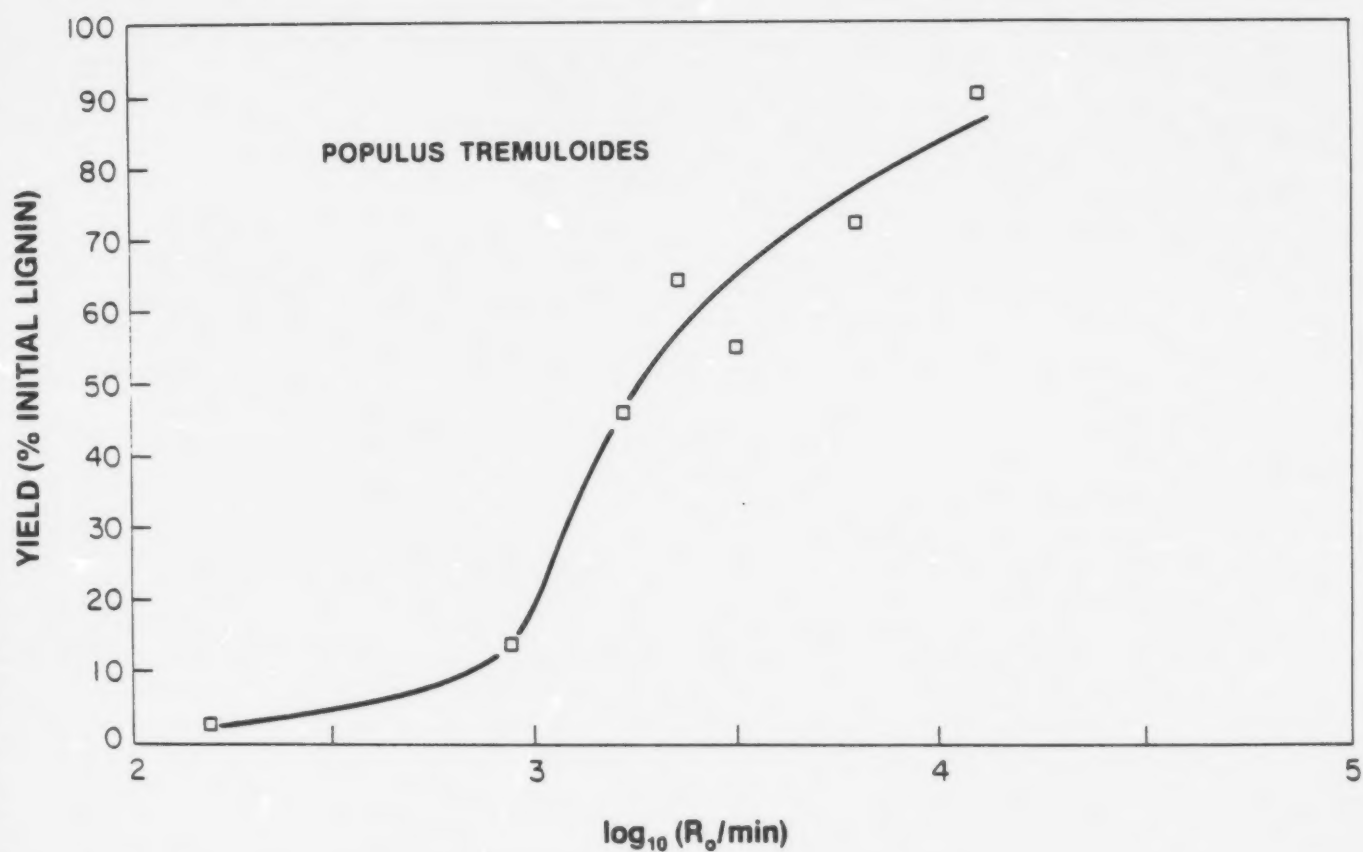


Figure 10. Lignin recovered as a precipitate following alkali extraction of the water-washed exploded fiber. The ordinate units are the ratio of lignin recovered (i.e. weighed) and the Klason lignin present in the untreated original wood

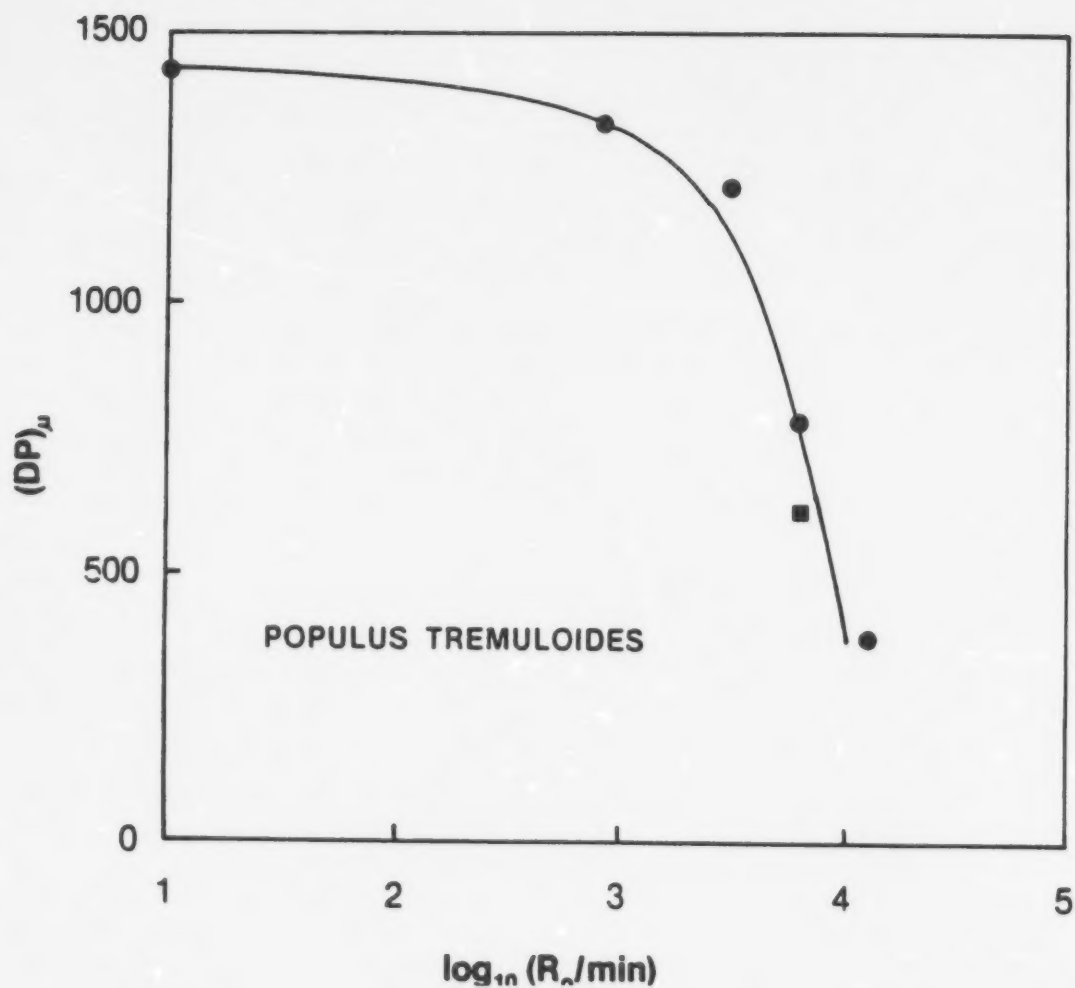


Figure 11. Degree of polymerization of the cellulose present in the water-washed, alkali-extracted exploded fiber as a function of treatment severity. The results at $\log_{10}R_0 = 3.8$ were obtained as repetitions conducted by two different analysts using the same viscosimetry method

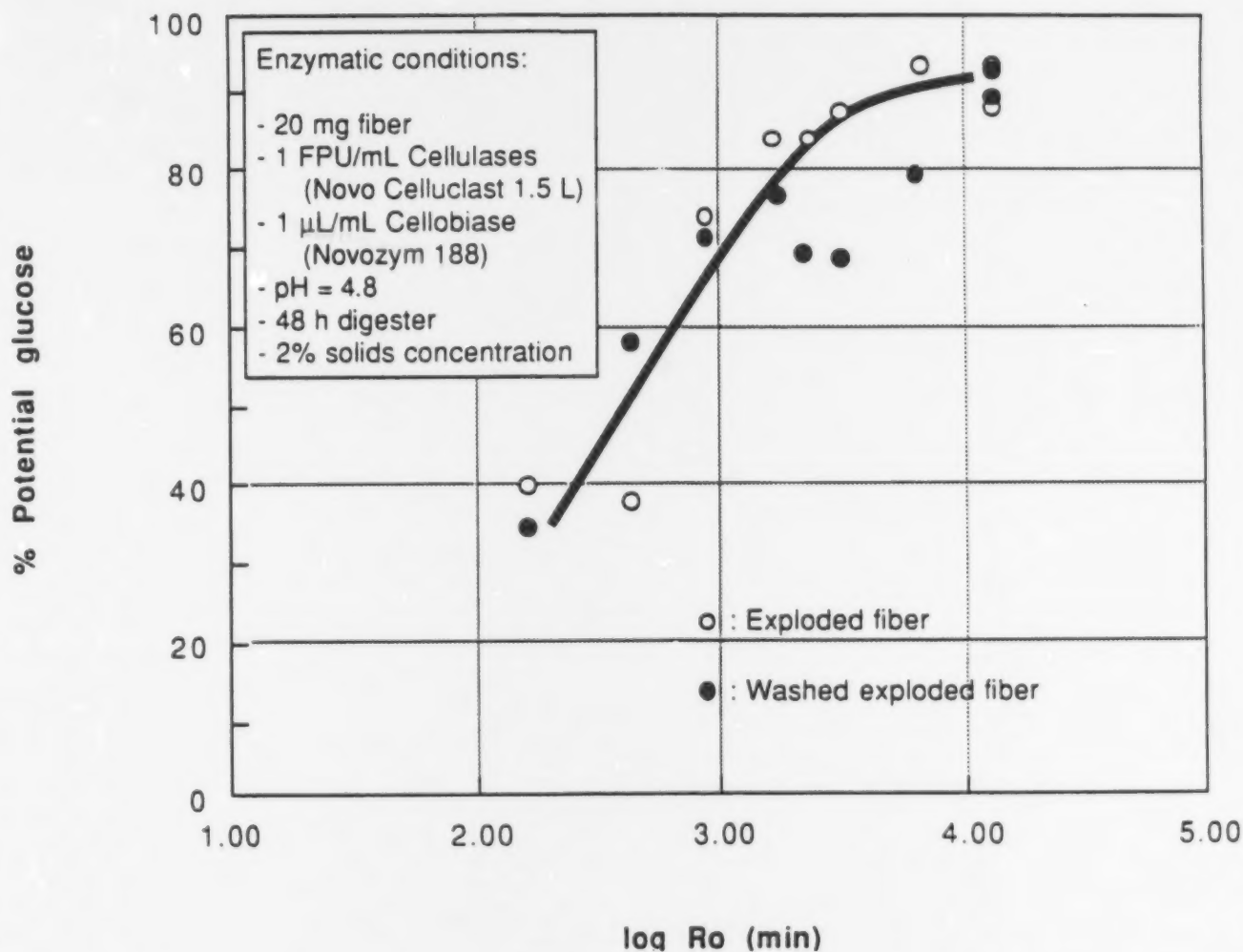


Figure 12. Enzymatic hydrolysis yields using as substrate the exploded fiber as a function of treatment severity. The ordinate units are the ratio of the glucose liberated enzymatically divided by the glucose corresponding to the holocellulose present in each treated substrate (Populus tremuloides)

SECTION C: STAKE POSITION PAPER ON SBC LIGNIN APPLICATION

by

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STAKE POSITION PAPER ON SBC LIGNIN APPLICATION

BACKGROUND

I. STAKE TECHNOLOGY PERTAINING TO BIOMASS CONVERSION LIGNIN:

Stake has been active in the research and commercialization of steam pretreatment of lignocellulosic residues since 1973. It has developed a proven equipment and process system capable of continuous steam treatment of wood and agricultural residues under high pressure. It has also developed or acquired state-of-the-art technologies in the processing and fractionation of biomass to cellulose, hemicellulose, and lignin. The company is currently actively commercializing technologies in various areas, including cattlefeed, chemicals, pulping, and wood composites.

Stake has successfully implemented its equipment and process technology at the commercial level in the chemicals applications (StakeTech Biomass Conversion, SBC, process). Currently, plants are operating at Kantvik and Kotka, Finland (xylitol from hemicellulose), Soustons, France (acetone-butanol from cellulose), Sherbrooke, Quebec (commercial scale research facility), Virginia, U.S.A. (ethanol from southern hardwood), and Minnesota, U.S.A. (demonstration plant). Being successful in its past efforts in developing high value products (xylitol and furfural) from hemicellulose, the company is recently aggressively exploring higher value applications for the lignin (and cellulose) fractions derived from the treated residues. Earlier studies on Stake SBC lignin have demonstrated its potential in several applications. A more rigorous approach has now been taken to follow up on such leads while pursuing other traditional and novel applications for lignin derived from various lignocellulosic residues.

II. POTENTIAL APPLICATIONS FOR STAKE'S SBC LIGNIN:

The current world supplies of Kraft lignin and lignosulfonate are estimated to be around 50 MM and 4 MM t/year. Recent R & D efforts have significantly increased the level of utilization of the pulp lignin, although annual lignin consumption is still only about 35 Kt of Kraft lignin and 700 Kt of lignosulfonate. The major problems encountered in lignin utilization attributed to the heterogeneity of lignin substrate (in functionality, molecular weight distribution, etc.) and a general lack of understanding and information on the performance properties of lignin (i.e., structure/ performance relationship). Similar problems are likely to be encountered in developing applications for biomass lignins. Although biomass lignin supply is insignificant at the moment, the US ethanol substitution program could lead to the annual co-generation of over 25 MM t of lignin (from the targetted 33.6 billion liters of ethanol) by 1990. A parallel situation will likely develop in Canada with the government attempting to

completely eliminate lead from gasoline. There is therefore tremendous incentives for developing novel applications for the lignin byproduct derived from biomass conversion processes. This position is further enhanced in that most of the Kraft lignin is generally burnt to recover the expensive pulping chemicals while the lignosulfonate supply is on the decline due to the phasing out of the sulfite pulping process.

Numerous reviews and economic studies have been reported in the past decades regarding the industrial applications of lignin. Most of the reports, however, deal only in generality with technical lignin derived from pulping (Kraft lignin and lignosulfonate). Very little technical information is available with respect to the properties of biomass lignin. Consequently, the potential uses of biomass lignin (and Stake's SBC lignin in particular) could only be extrapolated from corresponding studies using technical lignin.

The SBC lignin (and steam-exploded lignin in general) is believed to be superior to technical lignin in its lower molecular weight (with the desirable solubility in simple organic solvent); lower sulfur content, and higher reactivity to formaldehyde (less condensed). However, systematic characterization of the SBC lignin is currently still lacking and there is still considerable controversy over its properties. Moreover, the composition and properties of the SBC lignin derived are very sensitive to the substrate used and the precise steam treatment parameters, further complicating its characterization and application studies.

In general, lignin utilization can be grouped into two main areas: lignin as precursors to low molecular weight chemicals and lignin used as polymers.

1. LOW MOLECULAR WEIGHT CHEMICALS:

At present, vanillin, dimethyl sulfide (dimethyl sulfoxide) and methyl mercaptan are produced commercially from lignin. The feasibility of using Stake's SBC poplar lignin for the production of vanillin-syringaldehyde has been demonstrated. There is also considerable potential for producing low molecular weight chemicals from lignin. A unique feature of lignin is that it is enriched in aromatic structure and could therefore serve as substrate for producing aromatic chemicals, such as phenol, styrene, benzene, and toluene (starting material for a wide range of industrial chemicals using conventional technology). Current US production of the aforementioned aromatic chemicals from petrochemicals is estimated at 1137 MM kg, 3176 MM kg, 5148 MM liters, and 3924 MM liters, respectively, (1983). While the market is enormous, there is at present an over-capacity in the US chemical industry, and the prices of the aromatics remain depressed.

There is recent interest in lignin-derived liquid fuels (such as methyl aryl ethers) which could serve as a nonmetallic

gasoline blending agent and octane enhancer. Considerable research, however, will be needed before transportation fuels can be commercially produced from lignin.

The problem in the application of lignin in this market area lies mainly in the inability of current technology to depolymerize lignin and recover the desirable products effectively and economically. Although considerable work has been carried out to produce lignochemicals (particularly phenol) by chemical means, most of the processes are currently uneconomical due to the high costs associated with breaking down the lignin polymer and the relatively low yields of the desired products.

Recently a biological approach has been contemplated as a means of producing specific lignin breakdown products through lignin-degrading fungi (or bacteria) or their enzymes. An example of this approach is the production of phenolic moieties by enzymatic demethoxylation and hydroxylation reactions during lignin degradation. Major problems with the biological approach are the slow reaction rates and the undesirable degradation of the phenolic intermediates.

Ultimately, both the current chemical and biological approaches have to resolve the diversity of products expected to be produced due to the complex nature of the lignin macromolecules. To more fully exploit this area, it would be worthwhile to establish depolymerization methods which could result in a more "uniform" lignin substrate for subsequent processing. A combined chemical and biological approach may be worth considering by producing low molecular weight lignochemicals through chemical means (e.g., hydrocracking) and then subjecting them to biological catalysts to "tailor-make" certain desirable chemicals. Considerable R & D will be required before large volume lignin application in this area could be widely commercialized.

2. POLYMERIC LIGNIN:

Most of the current studies on lignin application have concentrated on exploiting the polymeric properties of Kraft lignin and lignosulfonate in large volume industrial use. There is still a general lack of technical information and understanding of property/performance relationship even with the technical lignin. Even less is known of the biomass lignin, including the SBC lignin. The potential markets for the SBC lignin are therefore speculative in nature, though the properties of the SBC lignin, as compared to technical lignin, are taken into consideration whenever possible. Ultimately it is intended that novel applications be developed for the SBC lignin based on its unique properties, instead of just using the SBC lignin as a replacement for technical lignin or petrochemical products currently occupying the market niches.

(A) Adhesives:

The current market for adhesives in waferboard and plywood industries in North America is estimated at around 680 MM kg/year. Recent studies at Forintek and Virginia Polytechnic Institute (VPI) have successfully demonstrated the replacement of 50% of the phenol in phenolic/formaldehyde adhesive formulation without adversely affecting the product quality. Based on this finding and assuming a 20% market take-over from conventional adhesive formulations, the potential market for lignin in adhesive application could reach 45 MM kg/year. Such lignin could sell for around US \$0.40-0.53/kg to make it attractive against petrochemical phenol (currently at US \$0.79/kg).

Both Kraft lignin and lignosulfonate are used as phenolic resin extender. While the molecular weight of phenol adhesives for wood gluing is generally in the range of 200-300, those of Kraft lignin and lignosulfonate average around 2000-3000 and 10,000, respectively. Such high molecular weights prevent good penetration at wood jointing surfaces and result in excessively high viscosity to lignin adhesive formulation. The molecular weight of the SBC lignin depends on the pretreatment and fractionation conditions, and has not been well defined. Earlier studies suggest that Stake SBC lignin has a Mn (number average molecular weight) of around 700 (the equivalent of 4 phenylpropane units). Gel permeation analyses also indicate that one-third of the SEL has a Mw (weight average molecular weight) of 1300 to 7000, while the rest has a Mw below 1300. This lower range of molecular weight of the SBC lignin may provide it with some advantages over the technical lignin in the adhesive application.

Reactivity towards formaldehyde is generally considered an indicator of the suitability of lignin in phenol adhesive formulation. It is now believed that high phenolic hydroxyl content is directly related to high formaldehyde reactivity, and phenolic hydroxyl content increases with decrease in molecular weight. Ultimately it is the molecular weight of the cured adhesives which determines the final strength property of lignin adhesives.

Technical lignin generally has poor reactivity toward formaldehyde because of the low phenolic hydroxyl content, higher ring substitution, and steric hindrance. The sulfonate groups are also known to deactivate condensation reaction of methylolated lignosulfonate in alkaline medium. Because of such deficiencies, technical lignin requires formulation with phenol resin to give adequate adhesive strength. Upgrading of the lignin adhesive strength property has been attempted by increasing the reactivity of technical lignin through chemical modification, such as demethylation and methylolating lignin prior to phenol condensation.

Stake's SBC lignin (and other steam-explosion lignin) has been widely believed to be more reactive than technical lignin. Hardwood lignin can be viewed as a mixture of coniferyl alcohol (with one reactive site) and sinapyl alcohol (unreactive) at a molar ratio of 1:1. Recent studies by the Batelle's group has shown that after Stake's steam-explosion treatment, the SBC lignin reactivity towards formaldehyde is equivalent to that of Kraft lignin (softwood lignin, predominantly coniferyl alcohol). This indicates that the Stake process has somehow enhanced the reactivity of the resulting lignin. It is anticipated that better results could be obtained with lignocellulosic residues with inherently higher lignin reactivity (e.g., softwood, grass, bark, etc.). The high solubility and reactivity of the SBC lignin will make the lignin more desirable as a coreactant for phenol and formaldehyde in phenolic resins, rather than just as a filler. The potential of using the SEC lignin in adhesive resins should definitely be further explored. If necessary, enhancement of the SBC lignin reactivity should be attempted. Both the chemical and specific biological (enzymatic) approaches to demethylation could be attempted to increase the phenolic hydroxyl content of the lignin products.

(B) Lignin Plastics:

The field of plastics include thermosetting resins, thermoplastic resins, and synthetic rubber and fibers. Thermosetting plastics account for 16% of the total US production of polymeric material, or 2790 MM kg in 1982. Rapid growth in the plastic market has been observed over the past decades, and the trends of plastic replacing metal and wood materials are expected to continue. Initial work with the use of lignin in engineering plastics has focussed on thermosetting resins. These are polymers formed through a curing or setting process by externally or internally generated heat and/or pressure. Once set, they cannot be softened by heat or solvent without degradation of the polymer. Although many thermosetting resins are currently commercially available, the phenolics, amines, urethanes, and epoxy resins dominate the market.

Polyurethanes are high performance polymers ranging from soft, flexible foams to hard, resistant coatings. It is now possible to make customized polyurethanes with specific properties by varying the urethane subunits. Urethanes are produced by the reaction of isocyanate with compounds containing an active hydrogen, usually polyols, polyethers, and polyesters. The current market for urethane polymers is around 450 MM kg/year.

Much work has been carried out on using lignin in the production of urethanes. Lignin contains active phenolic and aliphatic hydroxyl groups and can therefore react with

diisocyanates to form urethane. Recent work by Virginia Polytechnic Institute has successfully demonstrated the reaction of propylene oxide or ethylene oxide with lignin to obtain a polyol pre-polymer which can then react with isocyanate monomers for the production of urethanes. Such urethanes have properties similar to those obtained with conventional polyols. This finding provides considerable economic incentive for further development to replace normal polyol starting material (at around US \$1.65/kg) with lignin. Recent work has demonstrated that SEL (including Stake's SBC lignin) is the best among all lignin samples tested for producing the polyol pre-polymer. If the finding is substantiated, this could represent a high value outlet for biomass lignin, with a potential market estimated at around 14 MM kg/year.

Further work will be required to optimize the steam-explosion conditions to generate lignin for this particular application. The problem of the color resulting from lignin may also have to be resolved for wider product acceptance. Moreover, the actual cost savings using lignin may have to be clarified since a major expense in the process appears to be from the production of the diisocyanate reactant and not the polyol. Nevertheless, considering the potential market and value of the product, research and development in this application should be a high priority area in future exploitation of biomass lignin.

(C) Surfactant:

Anionic surfactant is currently the largest market for sulfonated Kraft lignin and lignosulfonates. In 1982, total US anionic surfactant market was estimated as 1389 MM kg (70% of the total surfactant market) at US \$0.73/kg. Lignosulfonates account for around 23% of all anionic surfactant, at US \$0.24/kg. Due to their dark coloration, their application is generally limited to the industrial surfactant areas, although various studies have been carried out to decolorize the lignin products for more general use.

It is believed that the surface active properties of lignin material, including water solubility and overall electronegative charge, is determined by the degree of sulfonation of lignin. Since biomass lignin can be considered as essentially free of sulfur (except when sulfur-containing catalysts such as sulfur dioxide are used in pretreatment), their application in this area will require introduction of sulfonate groups. Such an increase in product cost could likely make it non-competitive with lignosulfonates which are already established in the market.

Several new surfactant applications are currently being investigated for biomass lignin, including enhanced oil recovery (EOR, or tertiary oil recovery), and coal slurring.

Earlier work on Stake's SEC lignin has shown that steam-exploded poplar lignin can be readily modified to give derivatives which completely inhibit the adsorption of anionic surfactants on clay. These derivatives could therefore find application as low-cost sacrificial agents for enhanced oil recovery systems which involve surfactant flooding of oil bearing clay deposits. Treatment of these deposits with such an agent will allow a significantly larger proportion of expensive surfactants later injected into the well to mobilize more oil by emulsion. Biomass lignin will also have an advantage over technical lignin if there are higher value applications identified which require more uniform or more specifically modified lignin, then the initial lack of sulfur in biomass lignin would be advantageous over lignosulfonate to facilitate such synthesis. One example would be the production of ethoxylated lignin with desired water solubility which can then compete in surfactant markets not available to sulfonated lignin due to its properties associated with the sulfonate group (e.g., ionic charges).

(D) Dye Dispersant:

Currently Kraft lignin dispersants dominate the market because of their superior stability to dye formulation at elevated temperature. The reason for this is not known, but is probably due to Kraft lignin's adsorption properties as a result of its phenolic hydroxyl groups and unsaturated side chains. On the other hand, Kraft lignin has a tendency to stain textile fibres and reduce azo dyes, due to its high content of catechol and free phenolic hydroxyl groups. Improvement in dye reduction has been achieved by chemically blocking the phenolic hydroxyl groups.

More recently, new dispersants have been formulated from lignosulfonates possessing three unique properties: high molecular weight, high phenolic hydroxyl groups (for improved heat stability) and high degree of sulfonation (enhanced adsorption at high temperature). Current lignin dispersants out-compete petroleum-based dispersants by their low cost and superior performance. It is not known if biomass lignin will be able to establish a niche against the established Kraft lignin in this application. Further research should be carried out to test the technical feasibility, since the dispersant markets are high in value, though relatively small in volume.

(E) Carbon Black:

The carbon black market is relatively high in volume (1500 MM kg) and price (US \$0.73/lb). The main use is as a reinforcement for rubber to improve its tensile strength, and its tear and abrasion resistance. Lignin application in this

area has received considerable interest in the past, but co-precipitation methods studied so far have been technically unsatisfactory, non-economical, and not meeting the industrial needs. Recent work on "laundering" of Kraft lignin by repeated precipitation of lignin from acidic water at elevated temperatures results in the removal of low molecular weight or non-lignin components. This then prevents lignin agglomeration during the standard dry-milling process employed by the industry. At present, it is doubtful if the laundering process will ever be practical, since the process is extremely sensitive to the precipitation temperature at which lignin is isolated and the surface area of the resulting material. Overall, the important performance parameters include physical properties, chemical functionality, and particle size. Currently the carbon black industry has an oversupply problem and both the markets and prices are depressed. The significant research and development efforts required for biomass lignin to enter into this application area may not be justified.

(F) Asphalt:

The US asphalt market has ranged from 27 to 27.5 million tons/year (1963-1983) and is mainly used to make asphalt concrete as paving material. At present, practically all asphalt is produced from petrochemicals, but numerous attempts have been made to use lignin as asphalt extender. Lignosulfonates are found to be unsuitable due to their water solubility, resulting in swelling, leaching and low dimensional stability. Kraft lignin, on the other hand, demonstrates potential as a good asphalt extender. Recent work on lignin in emulsified asphalts also demonstrates that lignin can be successfully used in slow setting asphalt emulsion, but derivatization of lignin will likely be required for use in medium and fast-setting emulsions. When lignin is used as an anionic emulsion stabilizer, the compatibility of lignin (lignosulfonate) with asphalt is found to be inversely proportional to its sulfur content. Conventionally low sulfonated lignin is required for this application, or a partial desulfonation may have to be carried out. In this regard it is possible that the sulfur-free SDC lignin may be advantageous as a starting material. Recent work on SDC as an asphalt extender has demonstrated that a 30% replacement of binder has satisfactory aging and viscosity properties, but the ductibility is significantly reduced. In any event, this application should be considered high volume but low value (estimated at around US \$0.15/kg), and further testing is needed to explore its potential.

(G) Encapsulating Agents (Controlled Release):

The high adsorption/desorption property could be taken advantage of in the controlled release of agrochemicals or in

the feed industries. Lignin's polymeric matrix structure and its broad range of functionality enables it to entrap many biological active agents. The active ingredients are then released slowly either by diffusion through the lignin solid or through the degradation or dissolution of the lignin. The technique could be applicable for herbicides, pesticides, and fertilizers (particularly urea).

Several pesticides have been complexed with Kraft lignin through the formation of ester bonds to give controlled release biocides. Such a lignin-pesticide, sustained, release system has several advantages: ease in handling solids instead of liquids; reduced toxicity to humans and animals; control of the continuous release of active ingredients; lower risk of over application; and less frequent applications required. Although generally not considered, it is likely that the complexant could also result in stabilization of the active ingredients against leaching, degradation due to heat and light, and volatility. A Kraft lignin based system has been shown to significantly increase yields of soybeans and other crops.

Attempts have also been made to improve the complexing ability of lignin by cross-linking reactions, e.g., with epichlorohydrin or formaldehyde. Such modified lignin offers advantages over unmodified lignin in preventing specific interaction between the lignin carrier and the pesticide (which results in plasticization and causes problems in grinding and milling to granular or powder formulations). The modified lignin also does not require dissolution in organic solvents or concentrated aqueous alkali otherwise needed for unmodified lignin, thereby minimizing contamination of effluent with toxicant.

For the controlled release of agrochemicals to be widely accepted commercially, the process must be both simple and effective. It is believed that the active ingredient (such as pesticide) must be at least polyfunctional and the lignin polymer also polyfunctional rather than highly condensed. Other criteria include functionality, hydrophilicity, and glass transition temperature (T_g). Lignin with low T_g is shown to increase the undesirable interaction between the biocide and the polymer, and may therefore require modification to be carried out. It will be of interest to test the feasibility of the SEC lignin in this application. Considering that steam-exploded lignin is believed to be more reactive and less condensed than technical lignin, there may be an opportunity for a large outlet for lignin in the agrochemical industry.

The use of lignin for forming slow-release urea could be exploited in animal (cattle) feeds as well. Such lignin-coated urea could then serve as a continuous source of nitrogen (protein) for the ruminants. It will be interesting to test if Stake's SEC lignin could develop an application

in this area.

Lignin could potentially also serve as a sequester for micronutrients (such as Fe, Mg, Mn, and Zn) to be used for agricultural applications. In this area, lignin, rich in catecholic and sulfonate groups, is shown to have low complexing ability. Monocarboxylic groups (conjugated with aliphatic or aromatic double bonds) demonstrate slightly improved capability, but polycarboxylic compounds are most effective. Unfortunately at present, there is no process available to "tailor" lignin to be a better complexant than synthetic products, which currently dominate the market.

(H) Binders for pelletization:

The application of lignin as binders for pelletization represents a high volume and low value area. Lignosulfonate is at present the only lignin substrate used in this application. In 1986, the European markets for lignosulfonate consumption as binder for mineral pelletization, for organic material, and for animal feed are 50 Kt, 23 Kt, and 105 Kt, respectively. The corresponding North American markets are not available, but the overall application of lignin as binders likely represents a potentially large market as well. The steam-explosion biomass lignin could be advantageous to the lignosulfonate in that the lignin is essentially free of sulfur. This could then eliminate the desulfonation step required for lignosulfonate to be used in certain applications such as mineral pelletization.

Stake has previously explored the pelletization of steam-processed wood for cattle feed. The potential of stake processed material as binders in the pelletization of iron ore and coal fines has been studied. The present iron ore pelletization process uses bentonite which suffers from several disadvantages: increasing cost; high silica content (30.3%) of bentonite; energy required to remove bentonite; and low yield of iron. Stake's SDC lignin could offer potential advantages over bentonite in: no silica content; reduced energy for firing; increased iron yield; and reduced cost (if produced locally).

Another binder application for Stake's SDC lignin could be in coal pelletization. The potential market for lignin in this application could be huge. Considering the 90 MM t/y of coal mined in North America (3000 MM t/y world-wide), the coal fines could account for 135 MM t/y in North America (or 450 MM t/y world-wide). Coal fines are currently disposed of by blending with coal (resulting in a reduction of quality and selling price of the product) or as low value thermal coal. Pelletization of coal fines could improve the product quality by providing: ease of handling and higher selling price for pellets. It has been estimated that pellets will

sell at \$77/t or \$2.75/MM BTU as compared to fines selling at \$56/t or \$2.00/MM BTU). Recent work has shown that Stake processed wood results in an excellent pellet. Moreover, incorporation of limestone into pellets form has resulted in the trapping of 80-95% of the sulfur in the ash, thereby reducing sulfur emissions of the high sulfur coal. The potential applications of Stake's SDC lignin in both mineral and coal pelletization should be further explored.

Recently the overall applications of Kraft lignin and lignosulfonates have developed rapidly, as the knowledge of the lignin properties and performance becomes available. Biomass lignin is, at present, at an initial stage of commercial exploitation. Tremendous potential is present in various application areas. The above sections of lignin's potential market are not intended to be an exhaustive review of the area but rather to provide some basis for subsequent targetting of the areas to pursue. The tasks ahead will be to better understand the properties/performance relationship of Stake's SDC lignin and to develop market niches requiring its unique properties for industrial use.

III. APPROACHES TO DEVELOP NOVEL APPLICATIONS OF STAKE SDC LIGNIN:

The major problems currently encountered in developing lignin applications can be briefly stated as follows:

- lack of understanding of the complex and heterogenous lignin structure and functional properties;
- lack of information on property/performance relationship;
- diversity of potential application areas;
- lack of understanding of industry needs (process technology, multiple performance requirements).

In view of the technological challenges, it is essential to adopt an interdisciplinary approach to most efficiently develop applications for Stake's SDC lignin. A thorough understanding of the total performance requirement in any particular application area where the lignin product is intended to be used is absolutely crucial in the developmental work. Although a detailed approach to technology development is not possible at present, the general approach proposed is as follows:

1. Survey of lignin application areas (both literature and patent search). The initial phase of this process has already been completed, but the survey will be ongoing as new developments evolve or new opportunities become apparent.
2. Selection of tentative target application areas for further development work using SDC lignin. The selection will be based on our knowledge currently available on the performance required and the known properties of the SDC lignin. Previous assessment work on Stake SDC lignin will also be followed up to better define the application areas. The targets will be updated periodically to reflect the availability of technical information and test results.
3. Discussion with lignin industry (processors, suppliers, and end-users). This will establish or renew contacts with the industry in the targetted application areas to develop intimate knowledge of the current lignin-utilizing process technology and also the total performance requirements of particular lignin products. The objective will be to establish a working relationship with the industry to jointly develop designated processes and applications. Again this will be an ongoing process and subjected to modifications as the projects proceed.
4. Development of technical expertise. Concurrent to establishing industry ties, it is important to develop in-house technical capabilities as well as to identify external sources of expertise which are accessible when necessary. Since most of the current techniques involved in lignin analysis, fractionation, and modification are time-consuming and labor-intensive, it is necessary to be selective in the technical expertise to be developed. A

decision based on the cost-effectiveness and resource availability will also be made as to which types of characterization, fractionation, and modification should be carried out by outside experts established in the field.

5. Preparation of lignin samples for application assessment. Adequate quantities of SDC lignin from various lignocellulosic residues will have to be prepared for characterization, fractionation, modification (if necessary) and assessment. Decisions on the type of biomass, the treatment and fractionation conditions will depend on the targetted application areas. Once the initial assessment data become available, appropriate modification to the treatment and fractionation conditions will be made. Suitable lignin derivatization to enhance the desired properties might be attempted. The lignin derived from such technical manipulations will again be assessed. When positive results are obtained, it will then be necessary to produce larger quantities of the particular sample for "field-testing". To maximize the chance of success, all these activities will have to be closely co-ordinated with research organizations and the lignin industry to provide timely feedback during the joint development.

The above approach is necessarily very general in nature, but should form the basis for pursuing developmental work in lignin applications. The challenges in technological break-throughs and market penetration are not to be under-estimated, and the project will likely be medium-term and long-term in nature prior to successfully developing an acceptable product in the market. Nevertheless, the immense opportunities available for commercial exploitation should outweigh the risks involved. An interdisciplinary team of diverse experts, dedicated to the development of commercial applications for SDC lignin, together with active participation from the lignin industry (or lignin-utilizing industry) is likely to succeed in this endeavour.

SECTION D

DESCRIPTION OF THE PILOT PLANT STEAM EXPLOSION UNIT
LOCATED AT THE UNIVERSITÉ DE SHERBROOKE,
SHERBROOKE, QUÉBEC, CANADA

(June 1985 - August 1989)

Manager	: Paulo G. Koeberle, ing.
Technicians	: Jacques Bureau
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Research director	: Esteban Chornet, Ph.D.

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1. THE STAKE SYSTEM - OVERALL FEATURES

The University of Sherbrooke (UdeS) received a STAKE II feeder-digestor from STAKE TECHNOLOGY Ltd. in June 1985. The unit has a nominal capacity of 4 tonnes/h.

A schematic of the system is shown in Figure 1.

The system comprises:

- * The front end: raw material bin, auger and chute
- * The delivered STAKE II unit with the following subunits:
 - a coaxial feeder, which introduces the raw material into the digestor;
 - a digestor, which exposes the raw material to steam up to 3.2 MPa (450 psig) while the residence time can be made adjustable from 43 sec on. Typically the digestor is run at residence times comprised between 43 sec and 4 min;
 - a blow-valve, which discharges periodically the treated material during 0.3 sec with adjustable period duration typically set between 1 and 5 sec;
 - a high pressure 200 hp boiler, with a steam output of 7 GJ/h (6.7 MBtu/h);
 - a 20 hp hydraulic power system;
 - an enclosed control panel.

The discharge end constituted by a pipeline which conveys the product outside the building, using flashed steam as transporting media.

The system was installed on two floor levels in a rented space from one of Combustion Engineering buildings in Sherbrooke, Québec. The front and discharge ends were installed on the ground floor, as shown in Figure 2.

The STAKE II unit was installed in the basement, as shown in Figure 3.

A propane reservoir was placed outside the building, and connected to the boiler through appropriate piping.

2. DETAILED DESCRIPTION OF THE SYSTEM

2.1 Front end

2.1.1 Raw material handling

Originally, the raw material and product handling were essentially manual and extensive manpower was required to move feedstocks.

This obviated the need for some material handling equipment.

A 6.1 m long and 30.5 cm large steel reinforced plywood chain conveyor was designed and built in-house (Figure 4). It is powered by 1 hp electric motor.

The 4 tonne/h pneumatic conveyor (Figure 5), which uses a 23 cm line is an adaptation of a cereal centrifugal blower 122 cm in diameter, powered with a 20 hp electric motor.

Wood is fed into the blower vortex in a regular fashion by a special powered feeding bin (Figure 6) designed and constructed in-house.

A tripod with a manual crane (Figure 7) allows the handling of solids packed in large bags.

A small tractor (Figure 8) handles raw materials and products, as well as snow removal and other works outside the building.

The system has processed a great variety of feedstocks: municipal waste (MSW), paper refuse, cereal hulls, sugarcane bagasse, bark and hardwoods as well as softwoods. The mechanical properties of these materials differ widely and at times the feedstock bridges either in the raw material bin or in the vertical chute that leads to the coaxial feeder.

This bridging in the bin has been essentially eliminated by installing an agitation system, within the bin, comprised of a bar scraper and a sliding panel adjacent to the walls having a periodic up and down sliding movement thus disengaging the material sticking to the walls.

In the chute, where bridging occurs less frequently than in the bin, an automatic air blast system triggered by an infrared detector has been installed.

2.2 Work on the reactor

2.2.1 Coaxial feeder and choke cone

The coaxial feeder, key component of the STAKE system, is responsible for pushing the feedstock in the form of a compact and impervious plug, from atmospheric pressure into the digester which can be pressurized up to 3.2 MPa (450 psig). The operation is assisted from the inside of the digester by a flow-opposing conical end steel shaft which helps the raw material plug to stay compressed and tight-fitting.

It was originally designed to be manually displaced and to stay immobile in its last position. It required a great deal of attention from the operator, whose functions were to push the cone against the entering raw material whenever there were reasons to believe that the plug was becoming loose, and to retract the cone when it was too tight. The indicators were an ampere-meter hooked on the coaxial feeder motor, and noise or vibration from the coaxial feeder itself. A negligent control could lead to plug failure, with a so called "back-blow" which demands immediate action from the operator in order to prevent product inhomogeneity, and also stops the machine for 2 or 3 min.

The system has now been changed using our own design to a constant-pressure type actuation, and the cone can now move back and forth directly in response to the incoming flow requirements. The cone position is thus self-adjusting and the actuating pressure is usually set once, based on the coaxial feeder ampere-meter, and requires no further attention.

The hydraulic control system (Figure 9), is composed of a solenoid directional valve, a pressure control valve and a flow control valve.

2.2.2 Digester-screw adjustable bearing

At the early stages, one of the digester-screw bearings was changed from a fixed type to a position-adjustable type.

Abnormal noise and vibration during the first runs led to the discovery that the digester main material moving screw was touching the housing. Examination showed that the digester had worked some time under these conditions during its former ownership and the screw had already seriously weakened the reactor wall in a few places on the lower side. STAKE Technology Ltd was informed and immediately replaced the damaged housing with a new one. The screw

which had a few off-center portions, was straightened by grinding off the excess.

The same problem arose again a few months later and it was decided by our team to try and fix it without outside help. Another approach was taken this time. It was assumed that the screw bent due to its own weight and other mechanical stresses, but still within its elastic limit.

Installation of a special position-adjustable bearing was assumed to be the best solution. The bearing (Figure 10) was designed, built and installed solving the problem for three years. The problem then repeated itself, but a simple adjustment was enough to put the screw back to proper position.

2.2.3 SO₂ injection

The study of hydrolysis of lignocellulosics under acid conditions is conveniently conducted using SO₂ which can be easily injected into the digester together with the steam. This makes a good distribution of the acid easier to accomplish.

The system (Figures 11 and 12) uses a diaphragm pump to inject liquid SO₂ at a maximum flow of 18.7 kg/h against 28.2 MPa.

The SO₂ flow rate is measured via a load cell.

The liquid SO₂ from the 16 kg cylinder is precooled in an ice bath prior to reaching the teflon diaphragm pump which sends it to a vaporization coil located inside the stainless steel steam line which leads to the digester.

The disengagement chamber, return line and cold bath are necessary to prevent flow irregularity due to bubble formation inside the pump, and the vaporization coil is to ensure prompt SO₂ dispersion in gaseous phase.

2.2.4 Blow-valve control

Experiments to regarding optimization of steam consumption by adequate blow-valve operation obviated the advantages of introducing some sort of control to the blow-valve.

In October 1987, the blow-valve was equipped with a controller. Its input comes from the readings of an ampere-meter hooked on the discharge-screw motor.

The blow-valve trigger set-up uses three timers, each with a different discharge frequency, and the switching from the slowest timer to the fastest occurs as the discharge screw motor consumption readings increase.

The system is very simple, flexible and easy to set. Once set, it seldom will need any further change, and within a broad range of operating conditions it will always ensure maximum steam savings from over-blowing.

2.3 Discharge end

2.3.1 Discharge bin

The treated material which exits the digester is blown into a steel-framed, chemically treated, plywood receiver placed outside the building (Figure 13).

It enters through the top at one end and is discharged at the opposite end by a conveyor located on the floor.

The housing abates the strong discharge noise and delivers a product at about 60° C.

The bin volume is 15.2 m³ which makes it an intrinsically safe device against product blockage, and allows plenty of time for corrective action or shut-down, should a malfunction occur.

At the discharge end, the product is collected in bags, drums, handled by the tractor, or conveyed into an appropriate receiver bin.

2.3.2 Steam condenser

The STAKE discharge system was equipped with a process flash-steam condenser in order to study ways to reduce pollution, eliminate noise and recover essential oils and other volatiles.

The system uses cold water and has a steam-exposed area of 1.3 m² and it produces up to 3 l/min of condensate.

The condenser, shown in Figure 14, is made of 0.95 cm (3/8") stainless steel 304 tubing and has a total length of 42.7 m (seven 20 ft-lengths are used).

Steam is aspirated into the system by a blower located on the non-condensables exhaust side.

Cooling water is turned on and off by a solenoid valve which is actuated together with the blower.

The suction, made at the vortex of a cyclone keeps solids out and steam is allowed in, only if the suction is operating. This allows the condensation system to be turned completely on or off by a simple electric switch.

2.3.3 Product dryers

Three, free air, shelf dryers (Figure 15) were built to dry about 50 kg of product. The product drying is a necessity if it is to be stored for long periods without fermentation.

2.3.4 Product shelves

Two large racks of shelves (Figure 16), with a total available surface of 23.8 m², were constructed to store bags of processed biomass for later evaluation.

2.3.5 Sample freezer

In order to overcome any schedule mismatch between production and laboratory analytical work, especially for perishable samples, a 0.34 m³ freezer was acquired (Figure 17). It is used to freeze small samples of product, when drying is considered objectionable.

2.3.6 Product washing

The delivery of a washed product is in increasing demand, particularly for pulp and paper type experiments where it is desirable to remove the remaining chemicals such as sulfites.

Two stainless steel tanks measuring approximately 1m x 1m x 1.6 m have been installed for this purpose.

3 INSTRUMENTATION

3.1 Steam flowmeter

Material and energy balances on the STAKE system operation play an important role in the evaluation of process economics.

We equipped our reactor with a Vortex Shedding type flowmeter in order to directly measure steam consumption (Figure 18)

This type of flowmeter is a standard item and widely used in steam-flow measurement. It has a turn-down ratio of 15 and an accuracy of 1.5% of the read value.

Our flowmeter is a factory calibrated nominal 2", from YOKOGAWA ELECTRIC WORKS INC., model YEWFLO YF105-AG-P-B2A/S3S3°C.

The parts include the flowmeter, piping, temperature transducer NEWPORT 502A-K, pressure transducer YEWFLO # YA43-SB-S4, and flow totalizer YEWFLO # YFCT/1ST3/A1A*A.

Maximum flow is 4427 kg/h which is enough to measure the flow at the highest consumption levels.

In operation, the flowmeter presents problems due to interference from mechanical vibration on the pipeline. Improvements are required in order to shield it from vibration.

3.2 Thermocouples

Twelve thermocouples, type J, are installed on strategic parts of the digester.

Besides providing reliable information on the average operating temperature, they also allow detection of abnormalities such as poor raw material distribution and insufficient blow-valve cycling, allowing corrections to be made before they can cause serious disturbances.

3.3 Pressure gauges

Four pressure gauges connected to the digester provide reliable pressure readings, and like the thermocouples, they also provide quick information about any critical condition of product maldistribution inside the reactor.

4. DATA ACQUISITION

4.1 Computer

In order to monitor operating conditions there are several thermocouples and pressure gauges, a steam flowmeter, motor ampere-meters and rpm counters hooked on to an HP 9000 model 310 computer (Figure 19).

The data allows one to make reports and to back track and make diagnoses in case of a malfunction.

After the experiment, the collected data is processed and presented in the form of graphics (Figures 20, 21, 22).

4.2 Reporting

A spreadsheet was developed on a computer HP86 which processes information from our data acquisition system and provides information about the energy efficiency of the operation. A typical short report example is given in Figure 23.

5. STUDIES

5.1 Overview

The STAKE installation provides the opportunity for a variety of studies, which can be grouped into two categories:

- a) Studies performed on raw materials and products. Among the raw materials processed in our installation are: refuse derived fuel (RDF), oat hulls, sugar-cane bagasse, cellulose, impregnated woods for pulp and paper process tests, different kinds of bark and a variety of soft and hardwoods ranging from chips to sawdust.
- b) Studies and tests on different equipment variations in order to improve reliability, energy efficiency, and data gathering and develop new operating capabilities. Some completed experiments are: addition of SO₂, effect of discharge frequency on steam consumption (which lead to automatization of the blow-valve frequency setting) and experiments with raw material handling which allowed significant improvements on the front end of the system.

Some experiments still to be done are: maximization of shear effects at the blow-valve, explosion effect vs impact effect, raw material residence time distribution inside the digester, viability of volatile extractive production and energy efficiency optimization.

5.2 Study on steam consumption

The theoretical steam consumption of the STAKE process is easy to calculate, but in any process the real steam consumption is always higher than the calculated value due operation losses.

The 5 major steam **consumption** factors in the STAKE process are:

- A) Heat required to bring reactor from ambient to operating temperature (depends on operating pressure and temperature and occurs only during start-up);

- B) Heat losses through the walls of the reactor (depend on operating pressure and temperature);
- C) Heating of raw material to operating temperature (depends on operating pressure and temperature, raw material characteristics and flow);
- D) Make-up for short-circuited steam, that is steam that enters and exits without delivering useful heat (depends on operating pressure and temperature, raw material flow and discharge frequency);
- E) Steam leaks on packings, gaskets, etc. (usually very small, and will be neglected).

The major causes for losses are factors **B** and **D**.

Experiment planing:

The steam consumption factors outlined above can be identified and evaluated by the means we now have available, and what follows is a brief description of a series of experiments devised for this purpose.

First experiment - to evaluate factors "A" and "B": Heat requirement to bring reactor from ambient to operating temperature, and to determine heat losses through the walls.

This experiment will use no raw material and will be carried out with a shut blow-valve, the condensate being either discharged by the appropriate condensate-valve or kept under agitation by the digester screw.

A set-point will be selected and the system will be allowed to reach it while steam consumption will be registered, providing us with a graph of consumption vs time.

By examining consumption during warm-up and during steady-state at the set-point, we can calculate both the heat transfer rate of the system and the losses through conductivity.

Second experiment - to evaluate factor "D": Make-up for short-circuited steam.

This experiment involves a change in the blow-valve discharge period and will work on a fixed set of raw material flow, P & T and residence time. If the results of this test confirm what we observed in the first experiments with a flowmeter (E22) (Figure 24), we should be able to find a relatively broad zone on the lower discharge

end, in which steam consumption is low and relatively constant, depending only on solids flow and operating set point. Staying inside this low-consumption zone with the help of the automatic discharge blow-valve system, we eliminate one variable, making it easier to perform the next experiment which relates steam consumption with raw material flow.

Our preliminary results show that steam consumption can be diminished substantially by a systematic control of the operating frequency of the operating frequency of the blow-valve. The periodic short blows can be reduced to a point where the amount of short-circuiting steam (steam that enters and exits the system without actually releasing any heat) is negligible.

These results were already expected, due to former observations made on operating pressure drop after discharges under different discharge periods.

Third experiment - factor "C" - raw material flow vs steam consumption.

Different flows of raw material will be run under the same operating conditions, and the steam consumption will be measured for each flow.

Fourth experiment - factor "C" - P&T vs steam consumption.

These experiments, ran at a fixed raw material flow, on automatic discharge timing, will give us a STAKE steam consumption table for different temperatures.

5.3 Study on the mechanics of energy dissipation at the blow-valve level.

In May 1986, a rapid data acquisition system was installed on the discharge end pressure transducers, and pressure data was gathered at the frequency of 31.25 Hz. It was intended to give us an idea of the pressure transients occurring during discharge at the blow-valve level. These high pressure fluctuations, caused by the high differential pressure across the valve, can be responsible for the destructure that occurs in the wood.

The configuration of the valve opening and the passage located at the high velocity zone may have a crucial effect on the product's structural properties. This is also a zone where high and costly erosion occurs. An understanding on what occurs at this location could hold the key for a finer product quality control and bring the erosion cost to a minimum.

Figures 25 and 26 show some of the data from transducers located near the explosion zone extracted from a regular report. Our rapid data acquisition system was limited to about 30 Hz and less, which is likely to leave out a wealth of additional information.

In the report on this experiment the recommendation was made for the use of an oscilloscope as a better and cheaper analytical tool, and an oscilloscope model choice was made.

5.4 Data handling

A spreadsheet was developed in order to calculate the theoretical steam consumption of the steam explosion system, based on operating conditions, properties of the raw material and its moisture content. A theoretical steam consumption table was compiled and is presented in Figure 27.

6. MAINTENANCE WORK

6.1 Overview

The habitual maintenance work consists of lubrication and tightening of certain parts, mainly packings on moving parts.

A regular maintenance schedule was created for the system after thorough examination of the machine, and was put in the form of diagrams and check forms to be filled in.

Some of the diagrams and check lists as well as electric and mechanical schemes are shown below. This material is part of the system library and is kept in the computer memory, which makes changes and updating easy (Figures 28, 29, 30).

A dual function (TIG and arc) 250 Amp. welding machine (Figure 31) was acquired, which allows field erection of any kind of metal structure, as well as the fixing of parts and making of metal fillings at the site.

6.2 Repairs

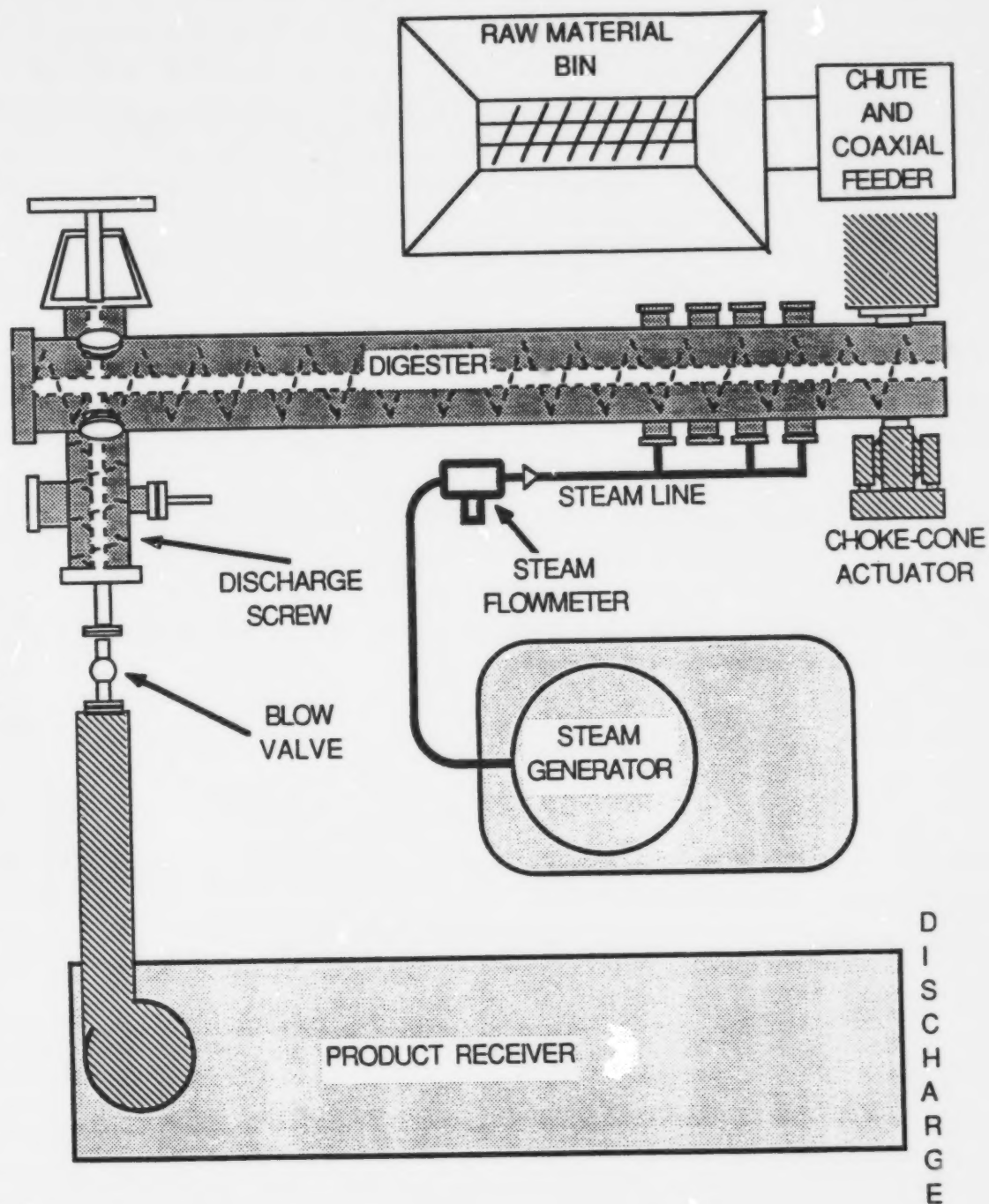
On April 1986, the choke cone fell off its support and was carried along by the digester screw and ended up jamming the discharge screw. Due to difficulties in getting materials for the machining of new parts, the old ones (Figure 32) were put back in place and the screwed-on choke cone was locked in place by a weld tack. A magnetic protection was installed on the screw motors to make them stop before any damage could happen in case of a similar event.

An elbow plate situated next to the blow-valve was severely eroded and starting to leak. The part had been already extensively repaired during former ownership and it was therefore replaced by a new plate. Erosion work on the affected part can be seen in Figure 33.

7. GENERAL CONCLUSIONS

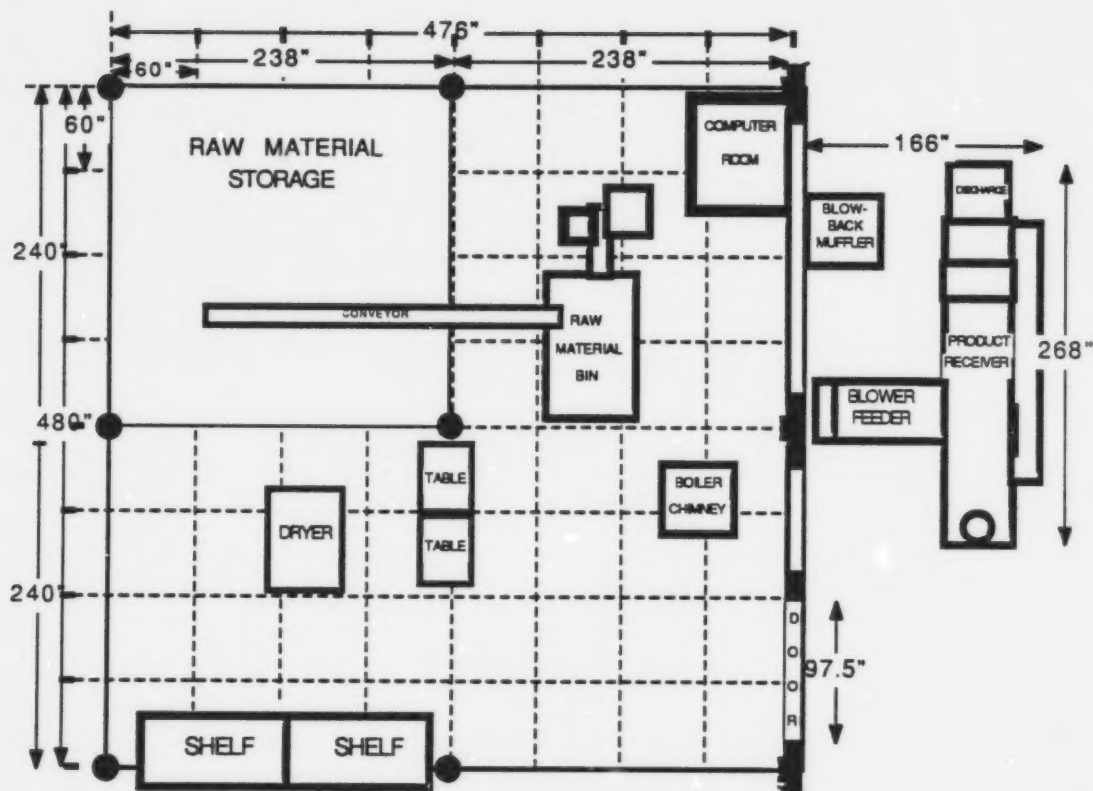
The STAKE II system installed at Sherbrooke has been thoroughly tested for pilot plant trials with diversified raw materials. Since its start-up in May 1985 and until September 1989, the number of operating days has been 62 for a total of about 400 hours of process time within the 160-230° C range.

The equipment has performed well throughout the experimental period. Temperature/pressure stability of the digester has been demonstrated, as well as product uniformity.



(Code: UWP-STK-SCHEMATIC JB.PK1)

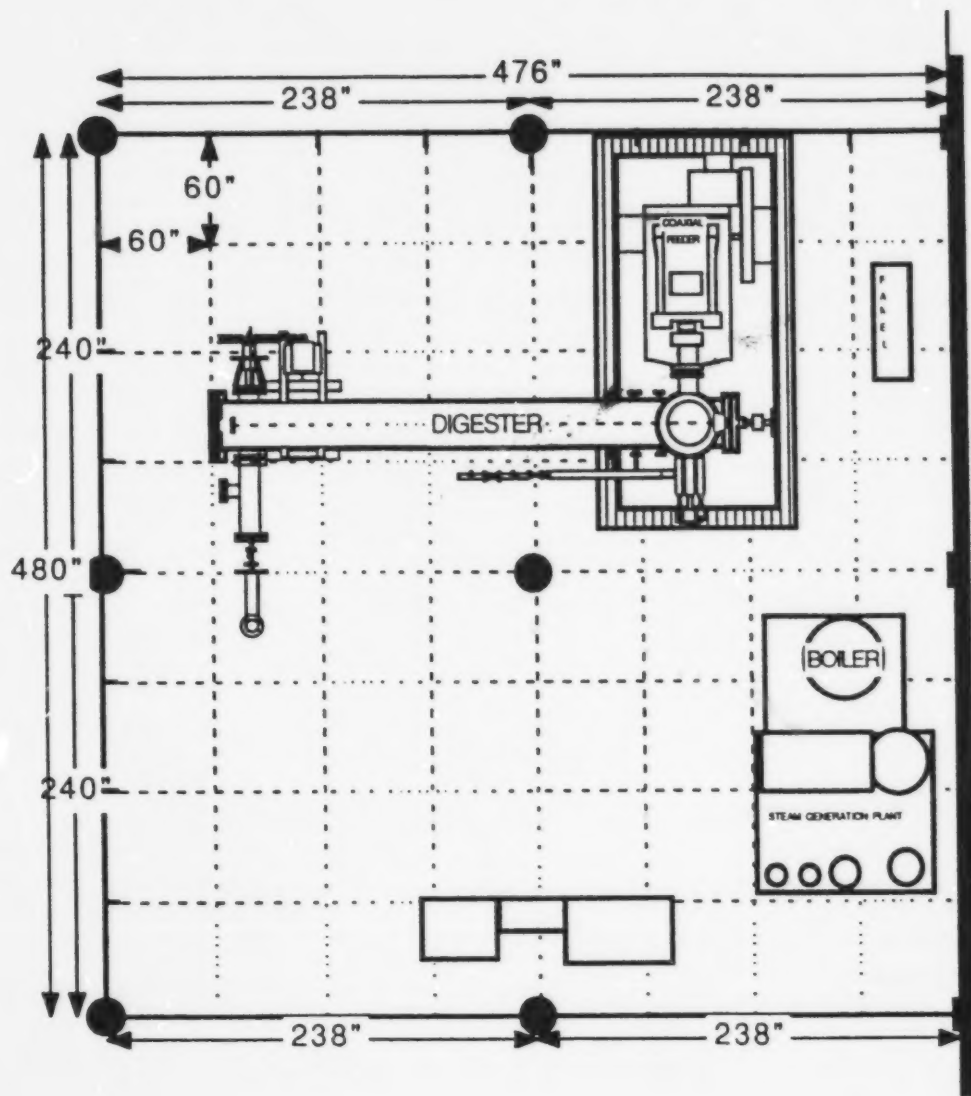
Figure 1. Schematic of STAKE II system at the Université de Sherbrooke (1986-1990)



(Code: UWP-STK-UPPER PICT 11)

Figure 2. STAKE II system at the Université de Sherbrooke: upper floor lay-out

(Code: UWP-STK-LAYOUT5 PICT LOW)



(Code: UWP-STK-LAYOUT5 PICT LOW)

Figure 3. STAKE II system at the Université de Sherbrooke:
lower floor lay-out

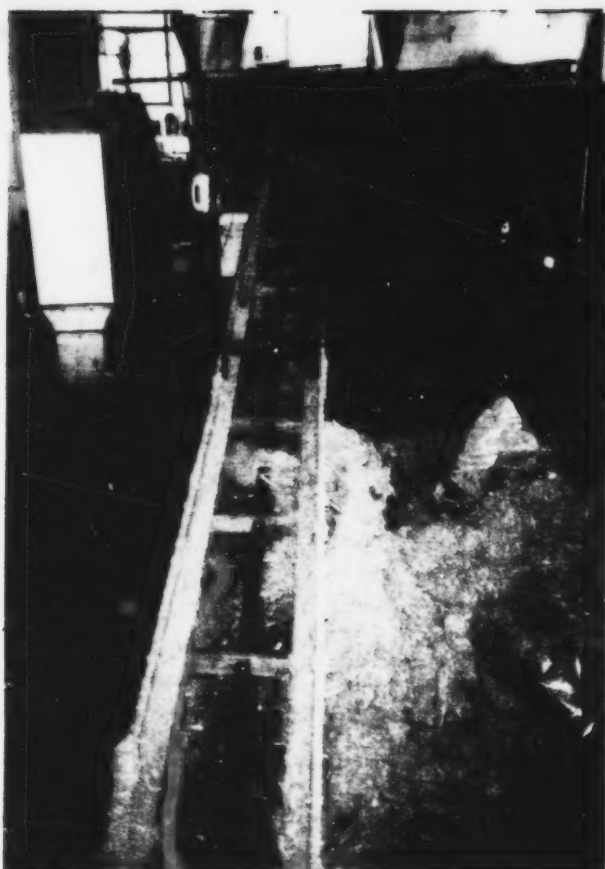


Figure 4. Chain conveyor

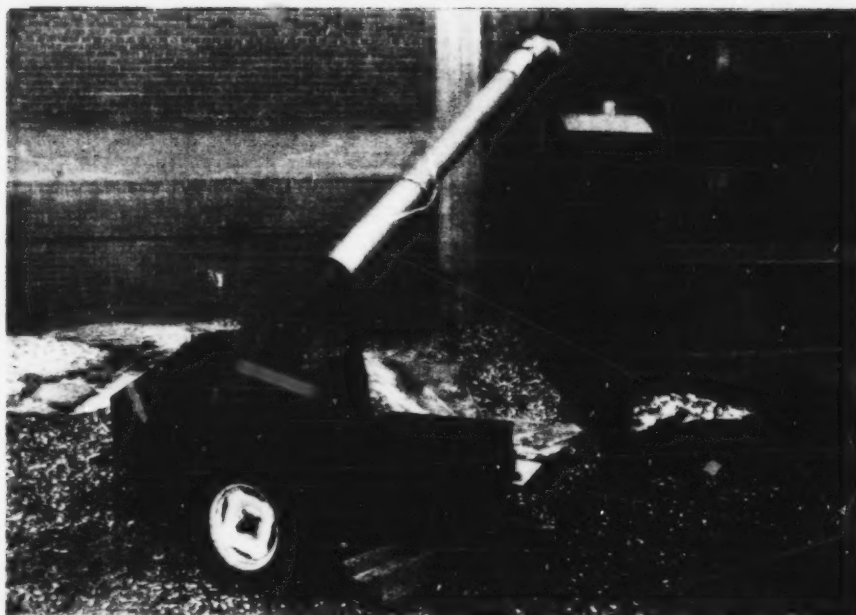


Figure 5. Pneumatic conveyor system: blower

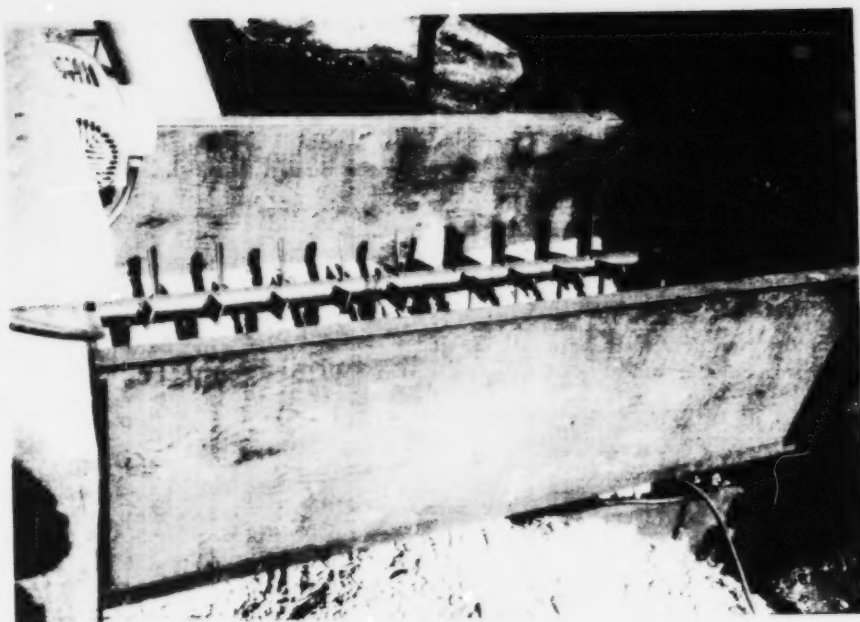


Figure 6. Pneumatic conveyor system: feeding bin



Figure 7. Tripod with a manual crane

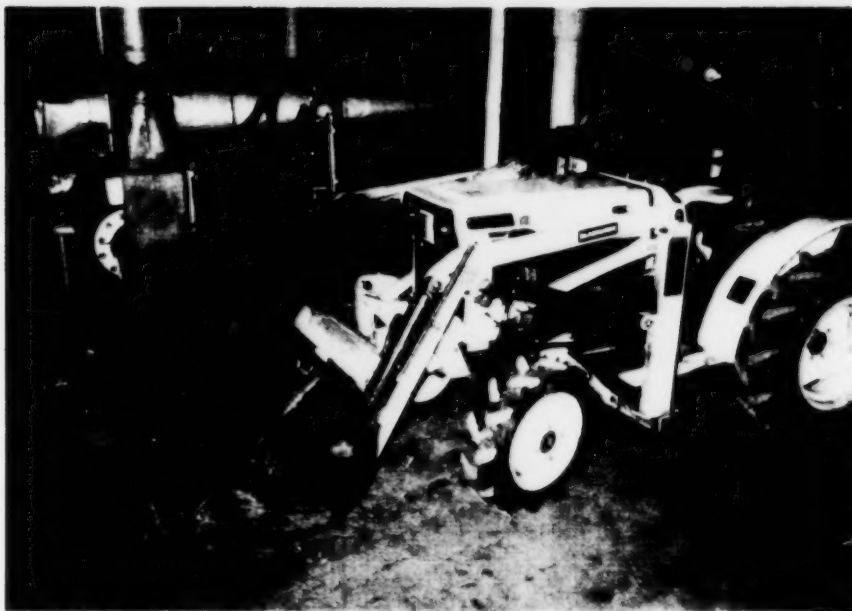


Figure 8. General purpose small tractor

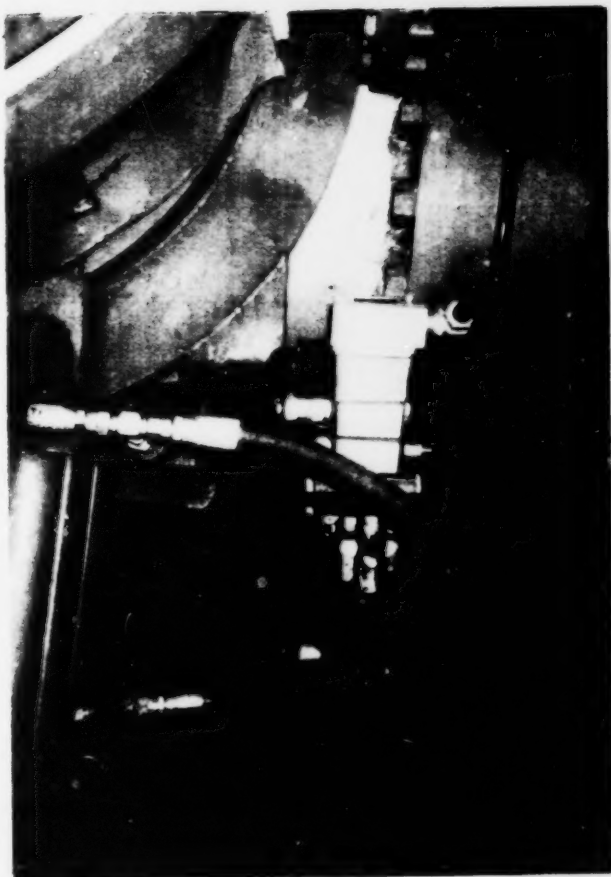


Figure 9. Choke cone hydraulic control system

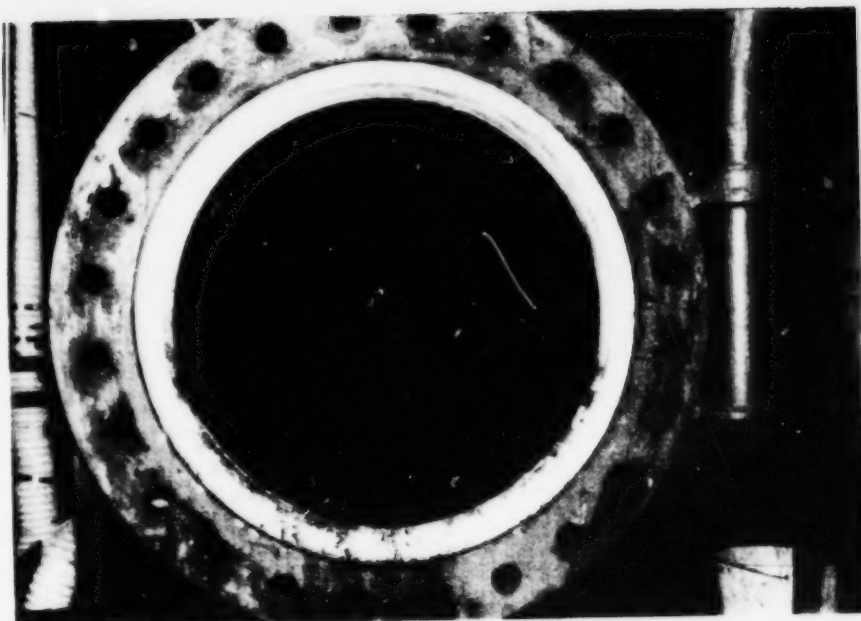


Figure 10. Digester screw: position-adjustable bearing

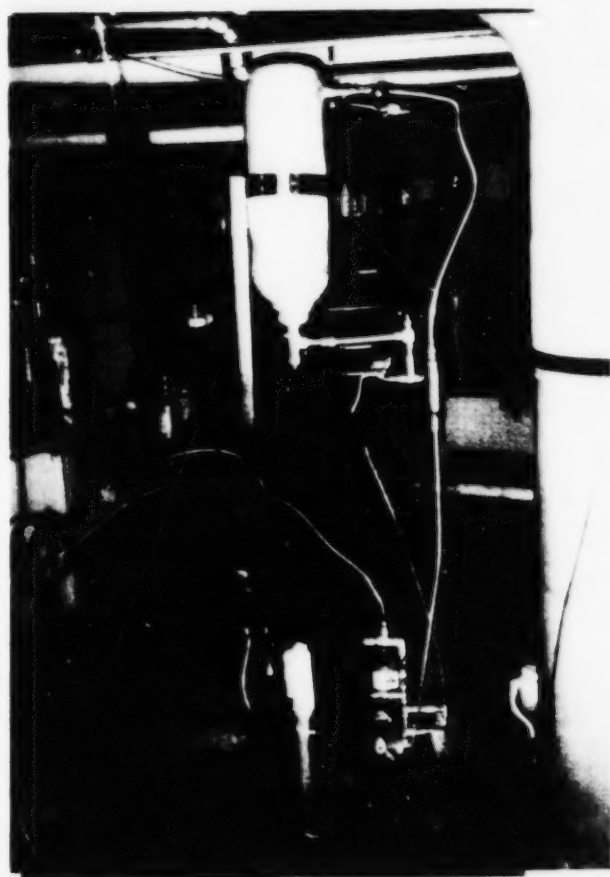


Figure 11. SO2 injection system: general view

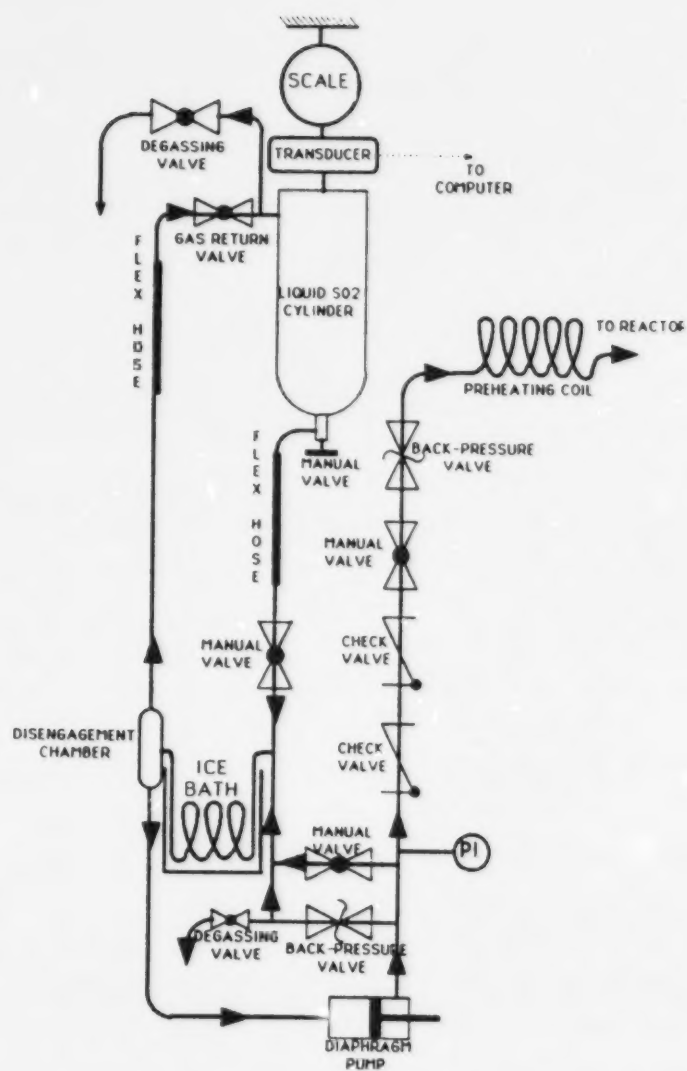


Figure 12. SO_2 injection system: Schematic

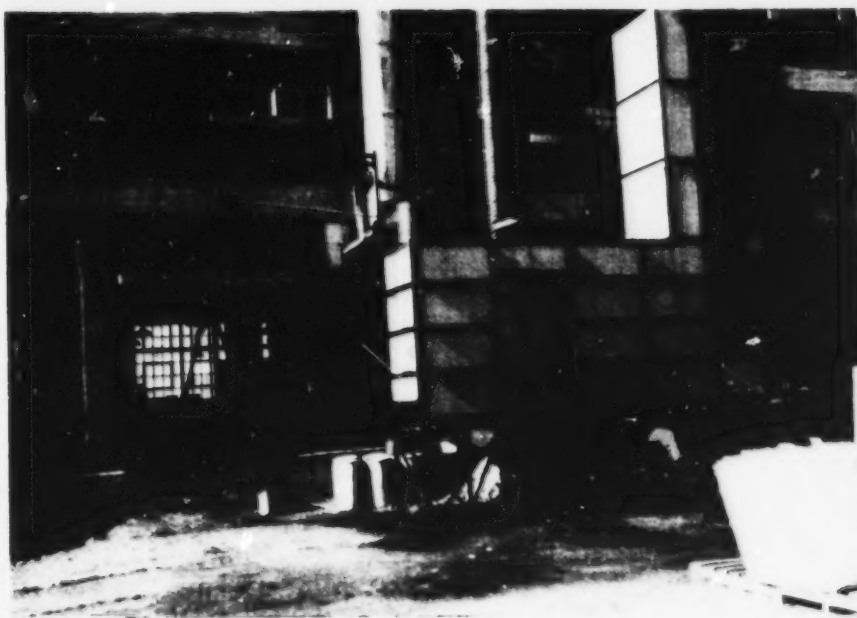


Figure 13. Product discharge bin

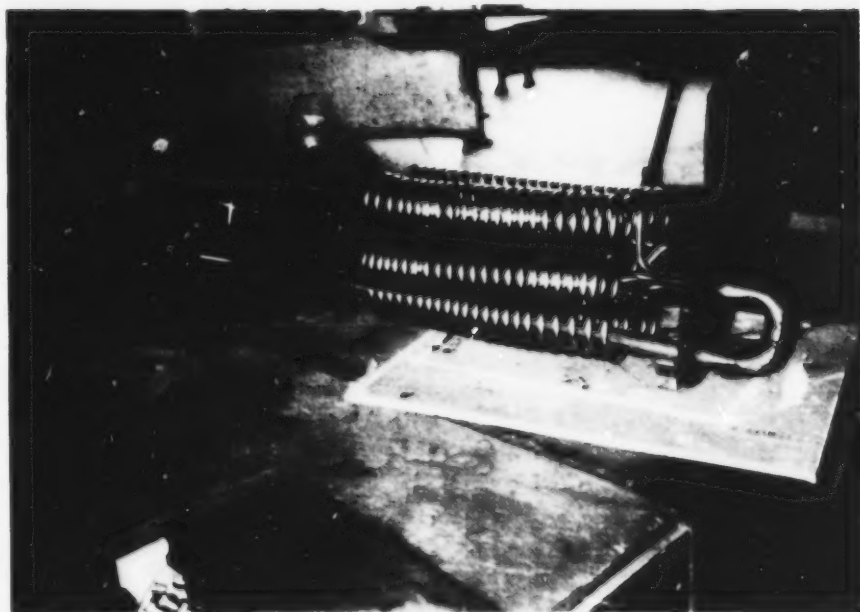


Figure 14. Steam condenser for sampling volatiles carried by the steam



Figure 15. Product shelf dryer



Figure 16. Racks of shelves

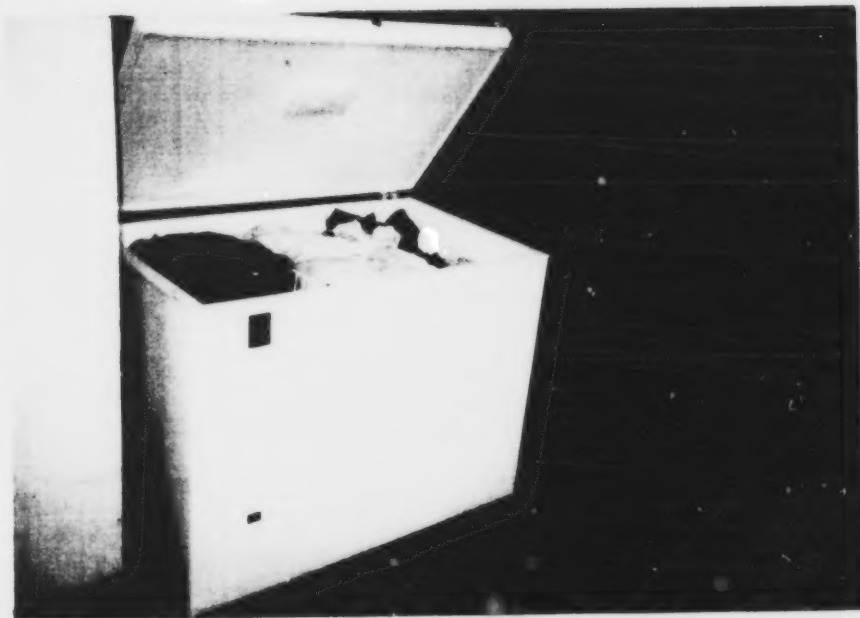


Figure 17. Sample freezer

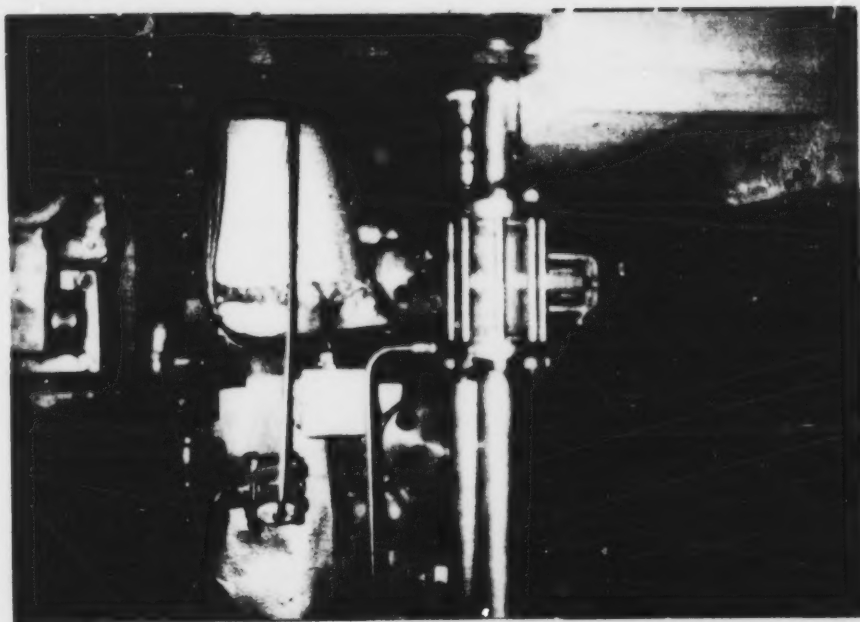


Figure 18. Vortex Shedding type steam flowmeter

CONFIGURATION OF THE DATA ACQUISITION/CONTROL SYSTEM FOR THE STAKE II PDU

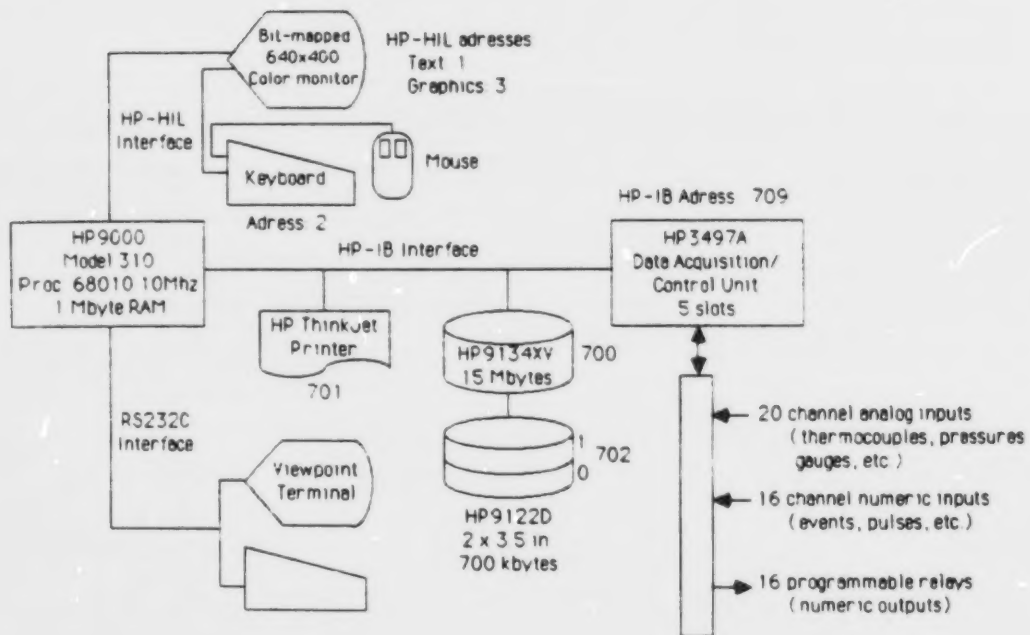
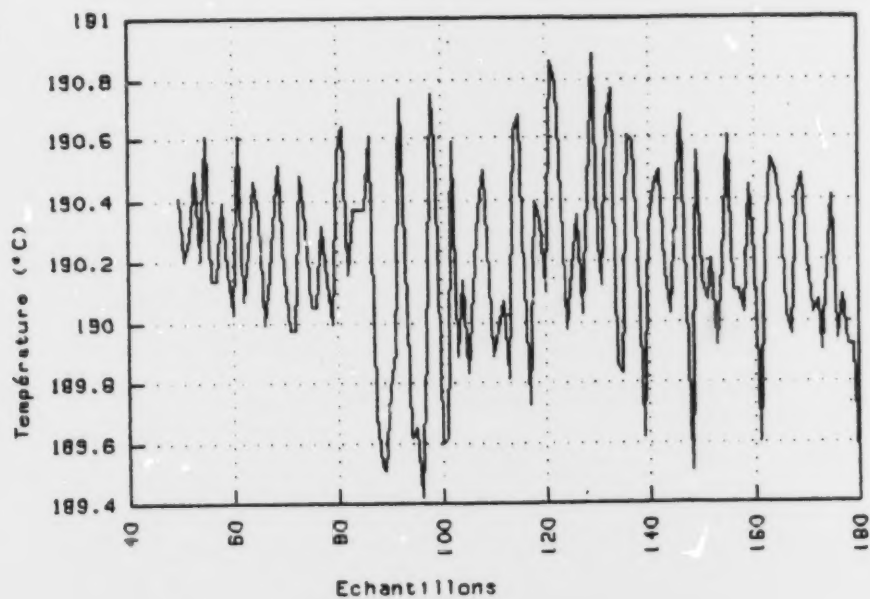
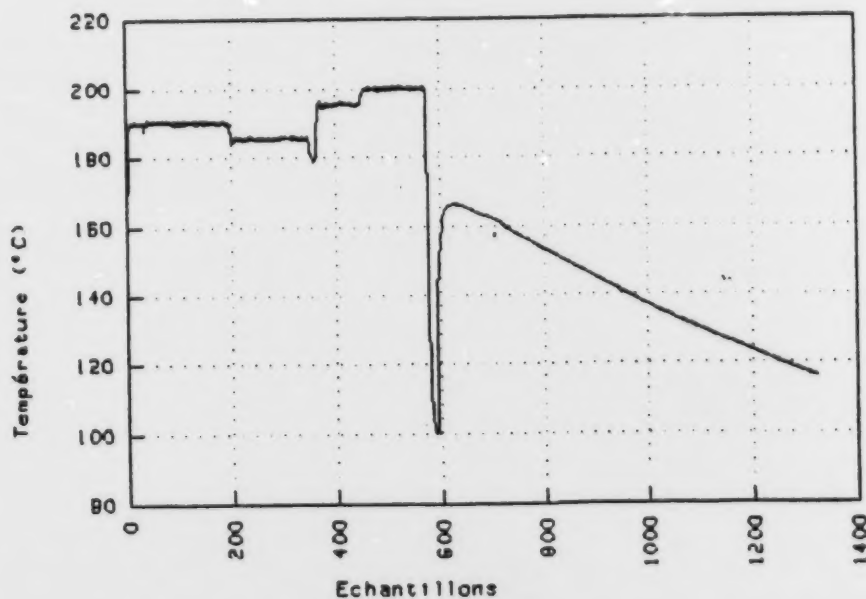


Figure 19. Data acquisition: computer

Statistiques en Y
MOYENNE= 190.193473269
ECART TYPE= .319542845877
VALEUR MINIMUM= 189.416785212
VALEUR MAXIMUM= 190.876983999



E19; 9/10/87



E19; 9/10/87

Figure 20. Data acquisition: presentation of temperature as a function of sampling sequence

ANALYSE PROGRAMMEE DES DONNEES:

EXP No. 880218_01

E26; STAKE-HYMAC; 18/02/88 (A B C - 1 2 3 4 5)

Canal no. 4 : JP.001 (Psi)

Echantillons 1034 a 1499 Période d'échantillonnage: 00:00:03

Statistiques en Y

MOYENNE = 129.086484666

ECART TYPE = .902927798532

VALEUR MINIMUM = 126.535584543

VALEUR MAXIMUM = 131.146503497

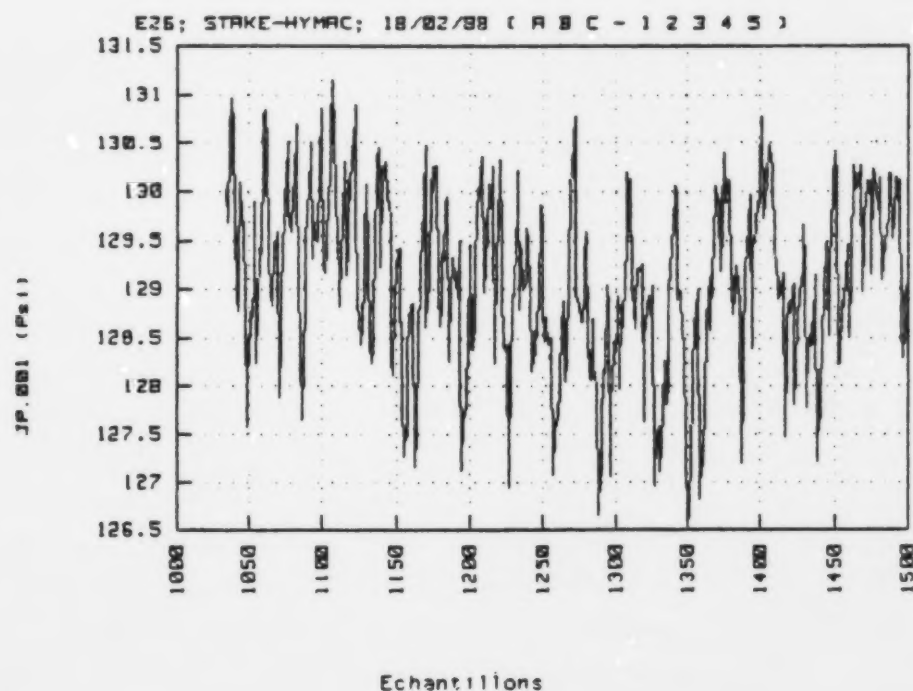


Figure 21. Data acquisition: presentation of pressure (sensor JP.001) as a function of sampling sequence

ANALYSE PROGRAMMEE DES DONNEES:

EXP No. 880427_01

E-28b; Peuplier tremble 322 Psi/220°C; Récup. vap.: 27/04/88

Canal no. 10 : VD.CMPT ()

Echantillons 680 a 1100 Période d'échantillonnage: 00:00:05

Statistiques en Y

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ECART TYPE = 264.278149474

VALEUR MINIMUM = 1476

VALEUR MAXIMUM = 2390

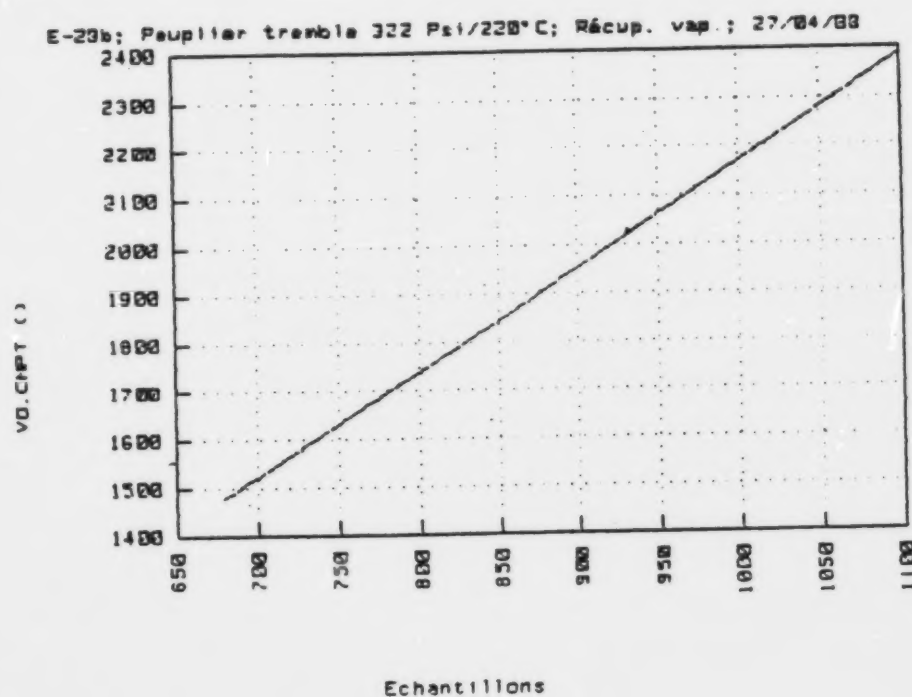


Figure 22. Data acquisition: presentation of cumulative feeding weight as a function of sampling sequence

INPUT

Raw material:	<u>Populus tremuloides</u>
Avg. Oper. Pressure:	324.8 psig
Avg. Oper. Temperature:	220.5°C
Residence Time:	120 s
Raw material moisture:	41.7%

OUTPUT

R ₀ severity factor:	7040 min.
Product moisture found:	50.0%
Heat losses	
• through system walls:	12.6% of minimum required steam
• due to steam shortcircuiting:	27.5% of minimum required steam
• from the boiler:	14.8% of minimum required steam
Stake efficiency:	71.4%
Overall system efficiency:	64.5%

Figure 23. Report on Visical spreadsheet for a typical experiment

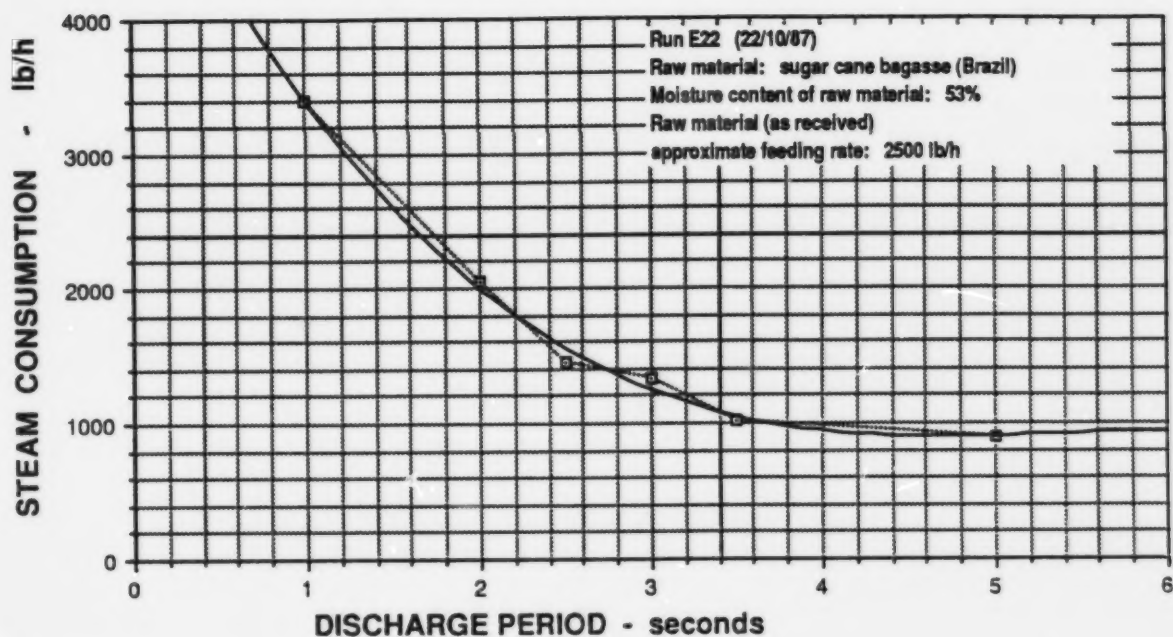


Figure 24(a). Steam consumption as a function of blow-valve opening frequency

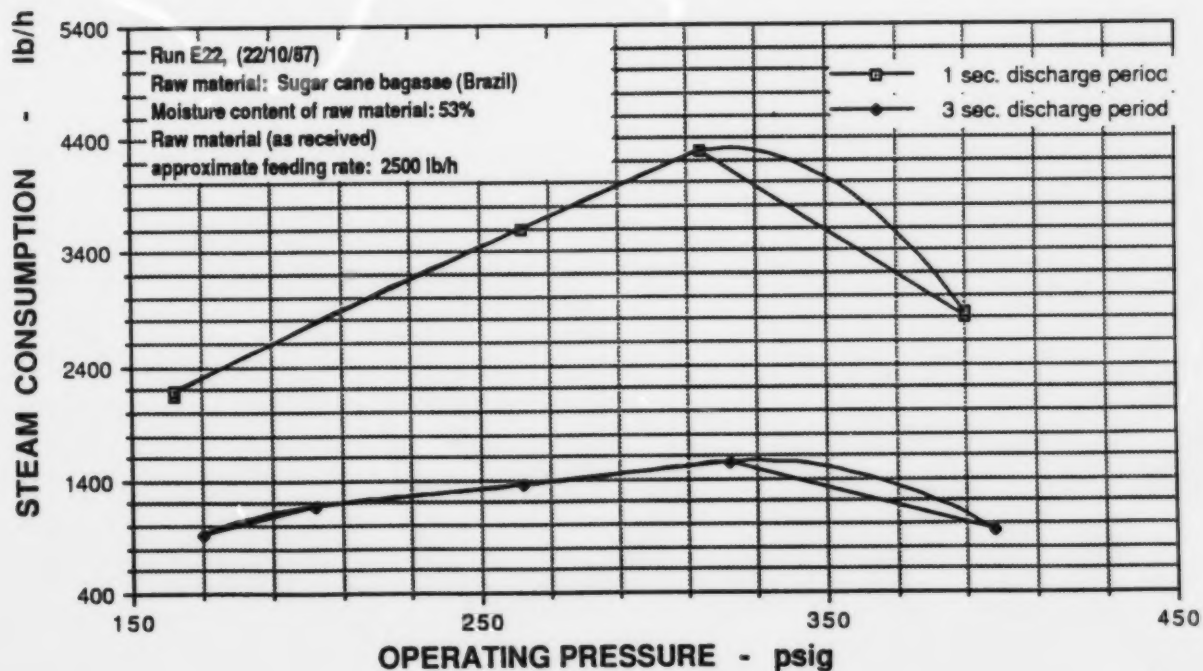


Figure 24(b). Steam consumption versus operating pressure

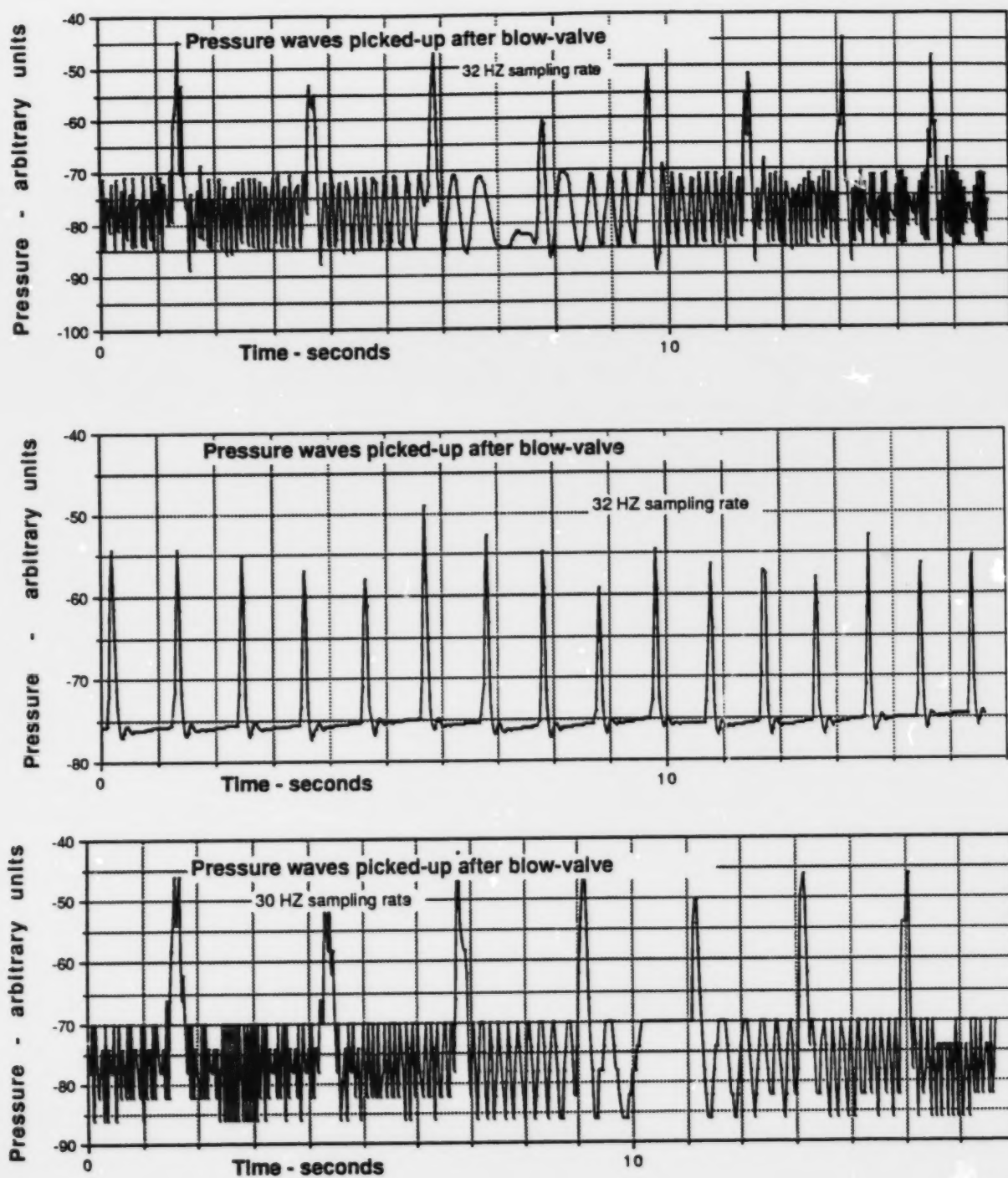


Figure 25. Pressure fluctuations at blow-valve level

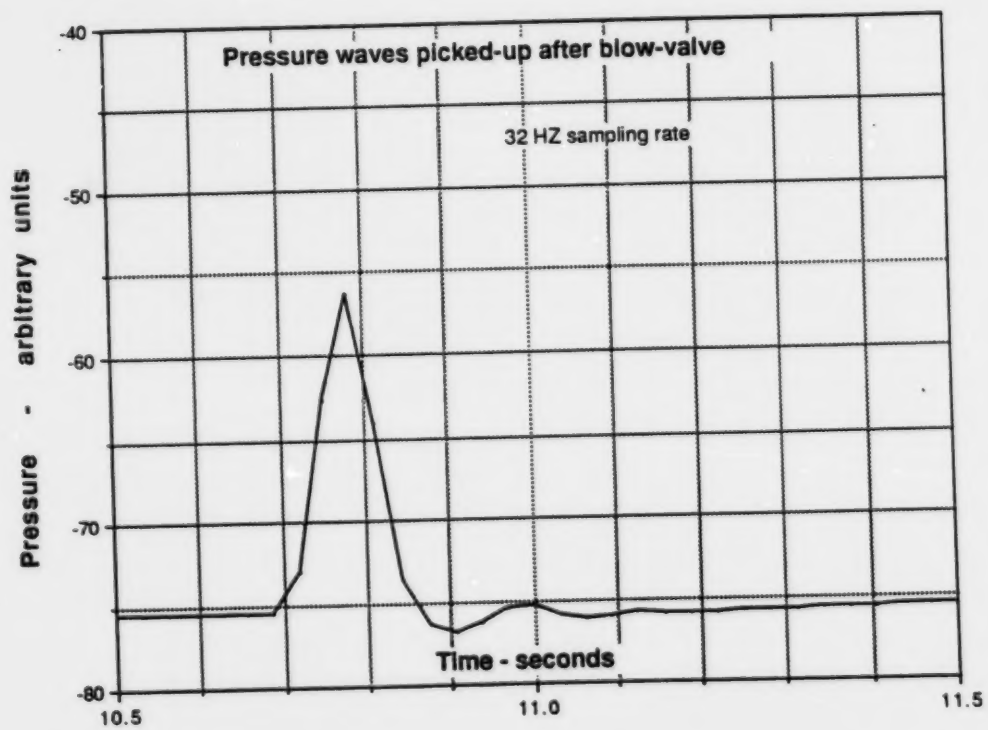
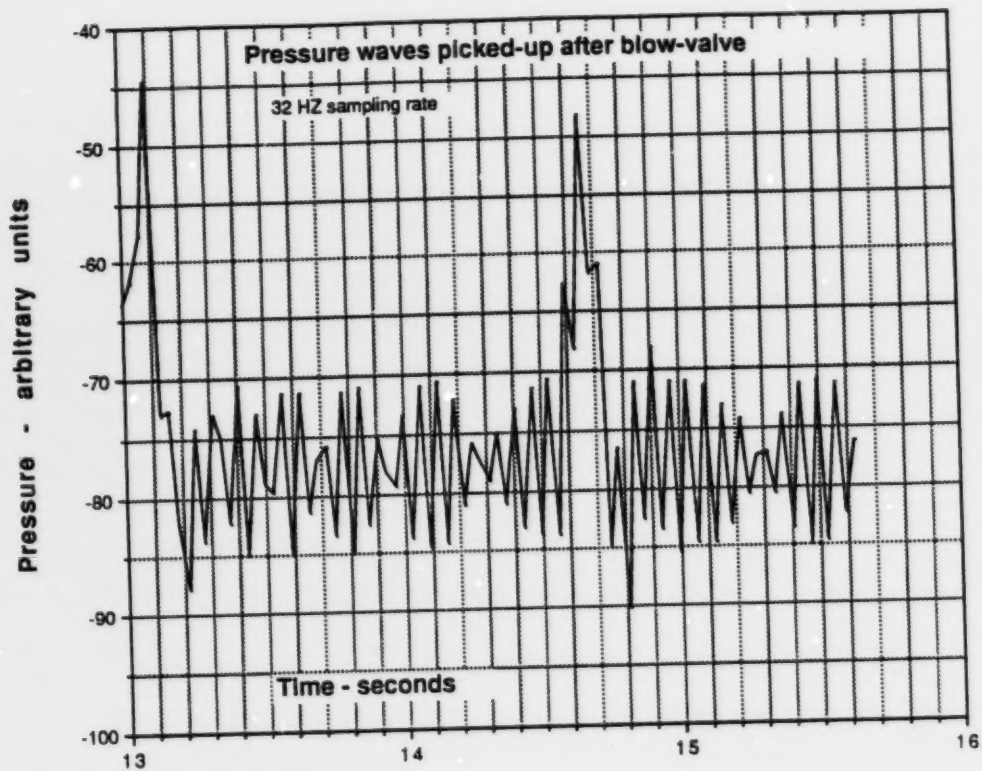


Figure 26. Selected amplifications derived from Figure 25

STEAM CONSUMPTION IN lb STEAM / lb DRY WOOD and PRODUCT MOISTURE AFTER FLASHING																
* = lb sat. steam at oper. T. / lb dry wood																
** = final product moisture																
%MOIST (WB)		0%	10%	15	20	25	30	35	40	45	50	55	60	65	70	75
T°C																
100	*	0.092	0.11	0.121	0.134	0.148	0.163	0.182	0.203	0.229	0.259	0.296	0.342	0.402	0.482	0.593
	**	8.39	18.1	22.9	27.7	32.5	37.2	41.9	46.5	51.1	55.7	60.3	64.8	69.3	73.8	78.2
120		0.115	0.138	0.152	0.167	0.185	0.205	0.228	0.255	0.287	0.325	0.371	0.43	0.504	0.604	0.744
		8.26	18	22.8	27.6	32.3	37.1	41.8	46.4	51	55.6	60.2	64.7	69.2	73.7	78.2
140		0.14	0.168	0.185	0.203	0.225	0.249	0.277	0.31	0.348	0.395	0.452	0.522	0.614	0.735	0.905
		8.09	17.8	22.6	27.4	32.2	36.9	41.6	46.3	50.9	55.5	60.1	64.6	69.2	73.7	78.1
160		0.166	0.2	0.22	0.242	0.267	0.296	0.33	0.369	0.415	0.47	0.538	0.623	0.731	0.875	1.06
		7.89	17.6	22.5	27.3	32	36.7	41.5	46.1	50.8	55.4	60	64.5	69.1	73.6	78
165		0.173	0.208	0.229	0.252	0.279	0.309	0.344	0.384	0.433	0.49	0.561	0.649	0.762	0.913	1.13
		7.83	17.6	22.4	27.2	32	36.7	41.4	46.1	50.7	55.3	59.9	64.5	69	73.5	78
170		0.18	0.217	0.238	0.263	0.29	0.321	0.358	0.4	0.45	0.511	0.584	0.676	0.794	0.951	1.17
		7.78	17.5	22.4	27.1	31.9	36.7	41.4	46	50.7	55.3	59.9	64.5	73.5	78	
175		0.187	0.225	0.248	0.273	0.302	0.335	0.372	0.417	0.469	0.531	0.608	0.704	0.826	0.99	1.22
		7.72	17.5	22.3	27.1	31.9	36.6	41.3	46	50.6	55.3	59.9	64.4	69	73.5	78
180		0.194	0.234	0.258	0.284	0.314	0.348	0.387	0.433	0.488	0.553	0.632	0.732	0.86	1.03	1.27
		7.66	17.4	22.2	27	31.8	36.6	41.3	45.9	50.6	55.2	59.8	64.4	68.9	73.5	78
185		0.202	0.243	0.268	0.295	0.326	0.362	0.403	0.45	0.507	0.575	0.657	0.761	0.894	1.07	1.32
		7.6	17.4	22.2	27	31.8	36.5	41.2	45.9	50.6	55.2	59.8	64.4	68.9	73.4	77.9
190		0.21	0.253	0.278	0.307	0.339	0.376	0.418	0.468	0.527	0.597	0.683	0.791	0.929	1.11	1.37
		7.54	17.3	22.1	26.9	31.7	36.5	41.2	45.9	50.5	55.1	59.8	64.3	68.9	73.4	77.9
195		0.218	0.262	0.289	0.318	0.352	0.39	0.434	0.486	0.547	0.62	0.709	0.821	0.965	1.16	1.42
		7.48	17.2	22.1	26.9	31.6	36.4	41.1	45.8	50.5	55.1	59.7	64.3	68.9	73.4	77.9
200		0.226	0.272	0.299	0.33	0.365	0.405	0.451	0.504	0.568	0.644	0.737	0.853	1	1.2	1.48
		7.42	17.2	22	26.8	31.6	36.6	41.1	45.8	50.4	55.1	59.7	64.3	68.8	73.4	77.9
205		0.234	0.282	0.311	0.343	0.379	0.42	0.468	0.523	0.589	0.668	0.765	0.885	1.04	1.25	1.54
		7.35	17.1	22	26.8	31.5	36.3	41	45.7	50.4	55	59.6	64.2	68.8	73.3	77.8
210		0.243	0.293	0.322	0.355	0.393	0.436	0.485	0.543	0.611	0.693	0.794	0.919	1.08	1.29	1.59
		7.29	17.1	21.9	26.7	31.5	36.2	41	45.7	50.3	55	59.5	64.2	68.8	73.3	77.8
215		0.251	0.303	0.334	0.368	0.407	0.452	0.503	0.563	0.634	0.719	0.823	0.953	1.12	1.34	1.66
		7.23	17	21.8	26.6	31.4	36.2	40.9	45.6	50.3	54.9	59.6	64.2	68.7	73.3	77.8
220		0.261	0.314	0.346	0.382	0.422	0.469	0.522	0.584	0.658	0.746	0.854	0.989	1.16	1.36	1.72
		7.17	16.9	21.8	26.6	31.4	36.1	40.9	45.6	50.2	54.9	59.5	64.1	68.7	73.2	77.8
225		0.27	0.326	0.359	0.396	0.438	0.486	0.541	0.606	0.682	0.774	0.886	1.03	1.21	1.45	1.76
		7.12	16.9	21.7	26.5	31.3	36.1	40.8	45.5	50.2	54.9	59.5	64.1	68.7	73.2	77.7
230		0.28	0.338	0.372	0.41	0.454	0.504	0.561	0.629	0.708	0.803	0.919	1.07	1.25	1.5	1.85
		7.06	16.8	21.7	26.5	31.3	36	40.8	45.5	50.2	54.8	59.5	64.1	68.6	73.2	77.7
235		0.29	0.35	0.386	0.425	0.471	0.523	0.582	0.652	0.734	0.833	0.954	1.11	1.3	1.56	1.92
		7.01	16.8	21.6	26.4	31.2	36	40.7	45.4	50.1	54.8	59.4	64	68.6	73.2	77.7
240		0.3	0.363	0.4	0.441	0.488	0.542	0.604	0.676	0.762	0.864	0.99	1.15	1.35	1.62	1.99
		6.96	16.7	21.6	26.4	31.2	35.9	40.7	45.4	50.1	54.7	59.4	64	68.6	73.1	77.7
245		0.311	0.376	0.414	0.457	0.506	0.562	0.627	0.702	0.79	0.897	1.03	1.19	1.4	1.69	2.07
		6.92	16.7	21.5	26.4	31.1	35.9	40.7	45.4	50.1	54.7	59.4	64	68.6	73.1	77.7
250		0.322	0.38	0.43	0.475	0.525	0.583	0.65	0.728	0.82	0.931	1.07	1.24	1.45	1.74	2.15
		6.87	16.6	21.5	26.3	31.1	35.9	40.6	45.3	50	54.7	59.3	63.9	68.5	73.1	77.6
255		0.334	0.404	0.446	0.492	0.545	0.605	0.675	0.756	0.852	0.967	1.11	1.28	1.51	1.81	2.23
		6.84	16.6	21.5	26.3	31.1	35.8	40.6	45.3	50	54.7	59.3	63.9	68.5	73.1	77.6
260		0.346	0.42	0.463	0.511	0.566	0.628	0.701	0.785	0.884	1	1.15	1.33	1.57	1.86	2.32
		6.81	16.6	21.4	26.3	31	35.8	40.6	45.3	50	54.6	59.3	63.9	68.5	73.1	77.6

Figure 27. Steam consumption in lb steam / lb dry wood and product moisture after flashing

SYSTEME STAKE CONTROLE ÉLECTRIQUE SCHÉMAS DE PRINCIPE

AUTOMATISME DES MOTEURS

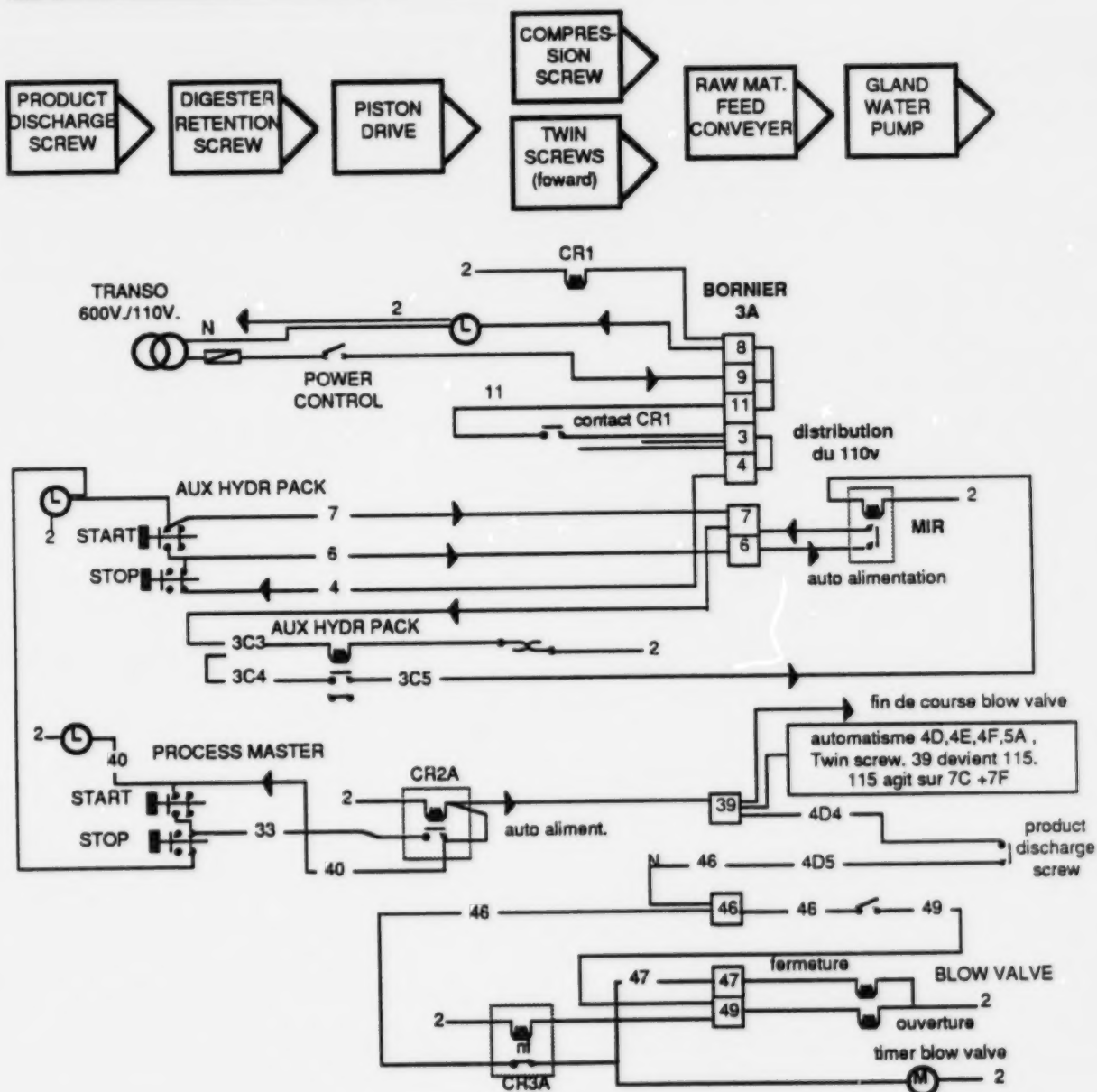
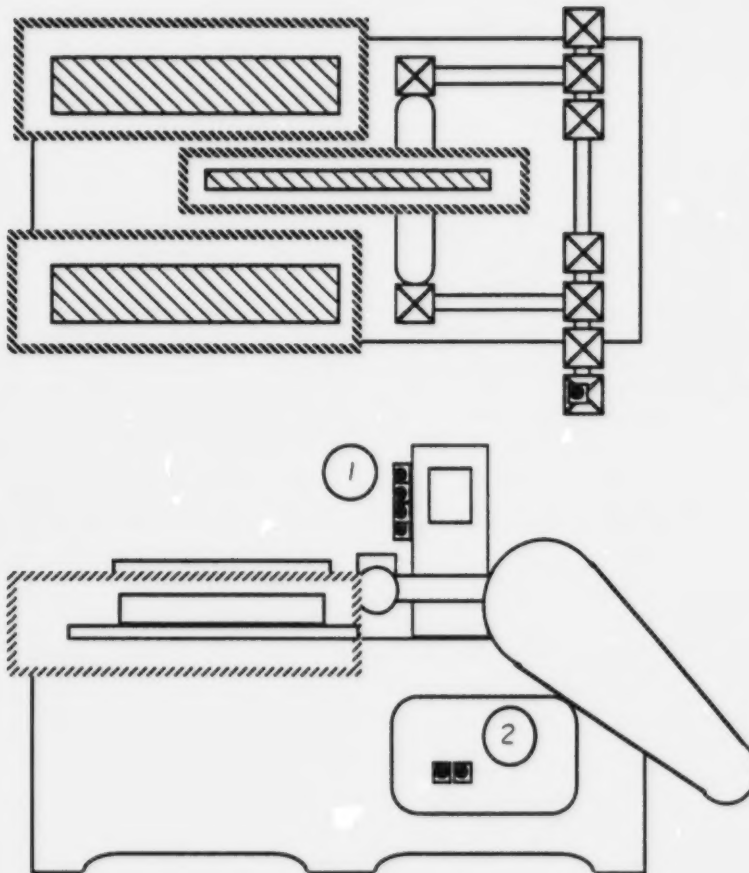


Figure 28. Maintenance Sheet

GLISSIERES

(Code: GLISSIERES A)



*1 AVANT CHAQUE UTILISATION

- Vérifier si il y a renouvellement de la graisse
- Donner 3 ou 4 coups de graisse avec le fusil a graisse

*2 A TOUS LES SIX MOIS

- Vérifier si il y a un jeu excessif de chaque coté des glissieres

Figure 29. Maintenance sheet

SYSTEME STAKE	ENTRETIEN	2
---------------	-----------	---

SYSTEME D'AIR COMPRI ME

VERIFICATION HEBDOMADAIRE					
DEFINITION	DETAILS	ENTETIEN VERIFICATION	REFERENCE	EFFECTUE LE	EFFECTUE PAR
FILTRES 1, 2, 3		NIVEAU D'HUILE	SCHEMAS 3		
RECEIVERS ET TRAPS		DRAINER LE CONDENSAT			
FILTRE à AIR		NETTOYER			
VERIFICATION MENSUELLE					
DEFINITION	DETAILS	ENTETIEN VERIFICATION	REFERENCE	EFFECTUE LE	EFFECTUE PAR
GENERAL		CHANGER L'HUILE			
FILTRES	à L'HUILE à AIR	VERIFIER			
VERIFICATION ANNUELLE					
DEFINITION	DETAILS	ENTETIEN VERIFICATION	REFERENCE	EFFECTUE LE	EFFECTUE PAR
GENERAL		RESSERER LES MONTAGES (boulons, vis)			
VALVES DU COMPRESSEUR	ENLEVER	NETTOYER INSPECTER			

Figure 30. Maintenance sheet

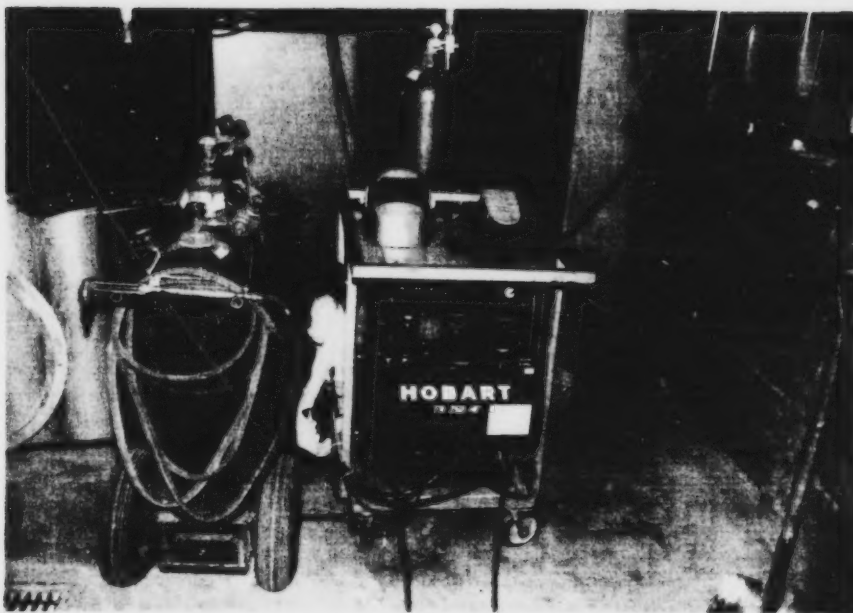


Figure 31. Welding equipment

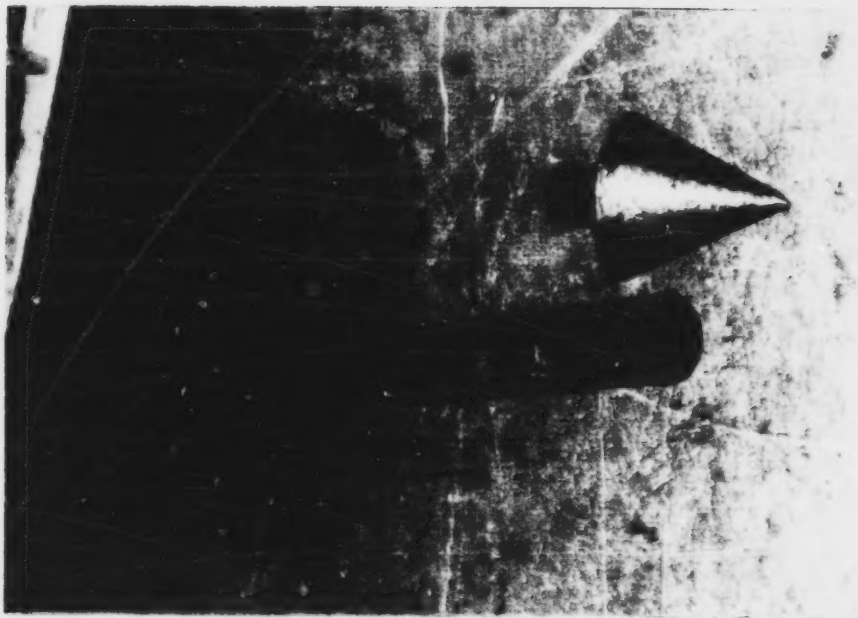
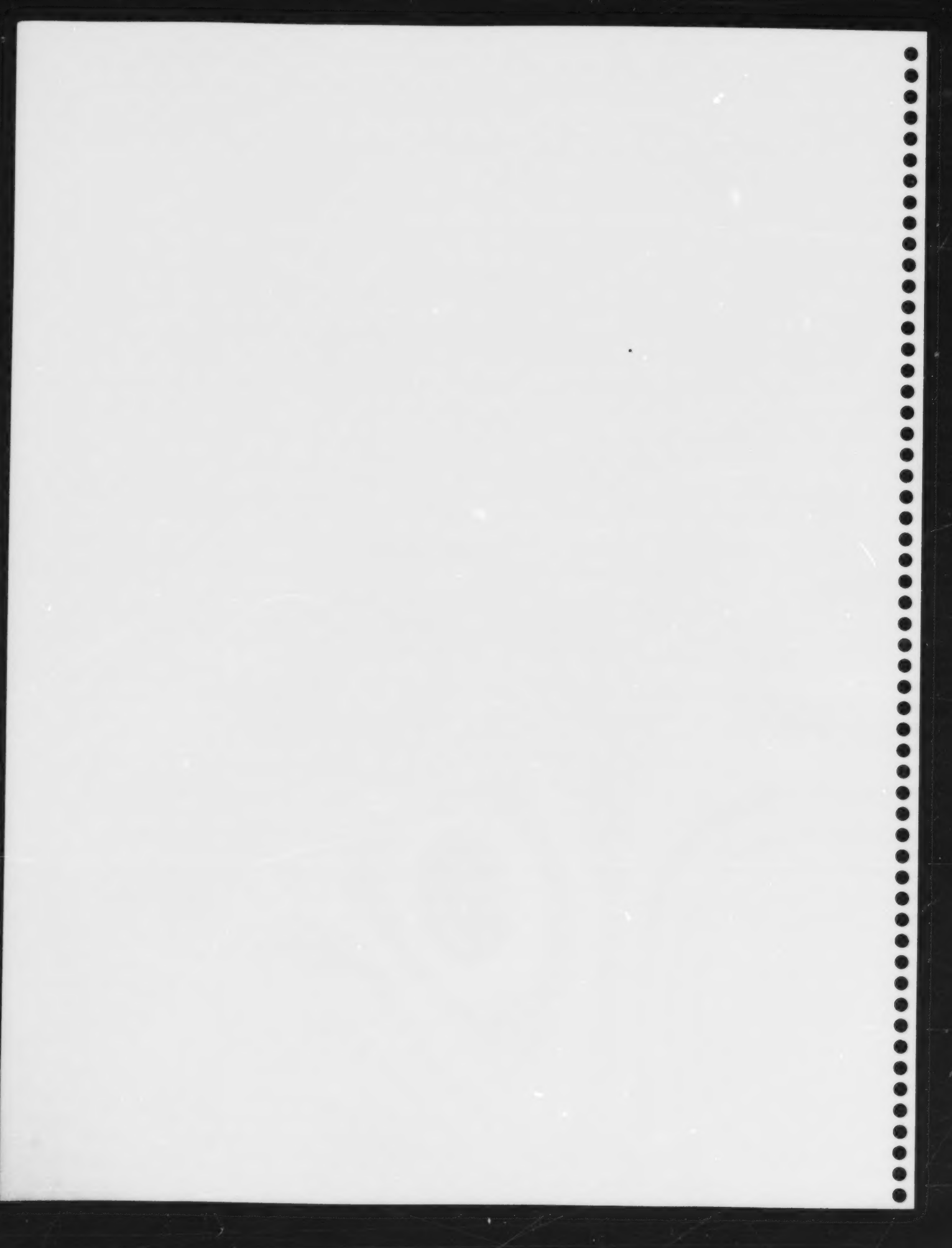


Figure 32. Old choke-cone parts



Figure 33. Erosion inside elbow facing blow-valve jet.



REPLIES AND REBUTTALS TO REVIEWER NO. 1

BY E. CHORNET

NOTE: replies are made to each of the points raised by the reviewer.

- The reviewer makes a comparison between the Sherbrooke experiments and the Souston's operation.

We need to comment on the comparison:

- in Sherbrooke we have treated bagasse, bark and wood (chips, shavings and irregularly shaped material).
Feeding each of the above materials to the digester has required some ingenuity and minor adjustments at the entrance of the coaxial feeder.

Each material having its own characteristics (density, flow patterns, ...) the operators must vary the peripheral equipment to facilitate the entrance to the coaxial feeder. Bridging can occur readily if the operators do not master the technology and the loss of the plug is inevitable if its consistency cannot be uniformly made.

Since the Sherbrooke unit is used as a research facility our operators are smart enough to overcome periodic difficulties. In a production line, as Souston was supposed to be, the needed adjustments are more difficult to make and perhaps this is the reason why they could not handle low density materials (i.e. straw) which require substantially different feeding conditions than wood chips.

- the discharge end of the reactor did create problems at the beginning of the experimentation but the operators rapidly understood the messages sent by the pressure, temperature and torque sensors and developed a routine to handle the build up of solids at the discharge end.

- We strongly disagree with the reviewer on the comments related to kinetics.

The reviewer has the candid perception that the lignocellulosic pretreatment (i.e. prehydrolysis) is to be treated as a homogeneous system.

The whole point of a single severity parameter is that it avoids the misconception of a single overall activation energy describing the extent of prehydrolysis.

The demonstration that $2 (T-100)/10 = e (T-100)/14.75$ is coincidental. In further articles, which the reviewer has not obviously had the

chance to consult, we have shown how a generalized reaction coordinate can be derived from the perspective of a non-homogeneous system. This implies that there is not a unique activation energy (and entropy!) describing the process, but rather a distribution of energies and entropies. We have also shown, in further articles, that the 14.75 value is not universal but it has to be determined from the experimental data sets.

In short, the reviewer and us have opposite views on the subject, which probably stem from a distinct understanding of kinetics of non-homogeneous systems.

- The introduction of an acid catalysed function in the severity parameter was done after the report had been written. It is a major piece of work, a copy of which is attached so that the reviewer can appreciate our thinking on the subject.
- On page A4 we have indicated that at high temperatures hydrolysis can occur via a dissociation of H_2O into H^+ and OH^- thus creating an increase in the concentration of H^+ by more than two orders of magnitude around the cellulosic polyelectrolyte.

We do not create an acidic milieu in the overall milieu but rather we change the double layer concentration of H^+ thus inducing a high H^+ concentration near the surface of the polyelectrolyte.

It is obvious that the overall milieu is neutral due to H_2O dissociation even it enhanced by temperature.
We have clarified this point in the text.

- On pA5 the reviewer objects to our explanation on a mechanical effect on dextrans. The reviewer should read our paper on the J. of Applied Polymer Science before trying to speculate on the issue. Mechanical effects do influence, within limits, the degradation rates of polymers in solution. This is well established.
- On pA10 the reviewer points out that the acid has an effect on severity which is not expressed in our R_0 definition. The reviewer is right on this matter and we have corrected the sentence appropriately.
- On pA16 - line 5: "To overcome heat penetration limitations ..." we have added the word limitations
- pA16- lines 3 and 4

The digestor used in the STAKE system uses a transfer screw which rotates the material while pushing it forward. There is good mixing

in the radial direction during each rotation. There is no mixing in the axial direction.

The radial mixing has as added advantage the fact that during each turn the material can be contacted with condensed water present at the bottom of the digester, since the latter is horizontally positioned. The material is then continuously and homogeneously imbibed with water if the operator maintains a given level of condensed water in the digester.

- pA16 - 2nd paragraph

The exact word is "soaking" rather than "swelling"

- pA16 - last 3 lines

The process conditions that we are suggesting are consistent in parts A and B and we do not see any major error in our choices of conditions and results given the biomass heterogeneity.

A $\log R_0 \approx 4.0$ gives us the general case for maximum pentosan recovery. Optimisation of the yield around this severity can then be conducted for each individual biomass.

- pA17 - $\log R_0 \approx 4.0$
- pA17 - 2nd sentence of conclusions

We know that the statement is controversial. However, we want to stick by it based in our own experiments in which:

- steam explosion treatment at controlled level of moisture has been conducted with and without impact.
- aqueous-steam treatment through orifices vs aqueous-steam treatment in enclosed autoclaves.

In all the cases the predominant effect is hydrolytic. Disaggregation and destructuring occur by two mechanisms:

- (a) in water-poor environments, the "pop corn" effect is the way by means of which the disaggregation occurs.
- (b) in water-rich environments (i.e. Trois-Rivières/Valade paper) the impact is necessary to disaggregate the chips.

- pA17 - Overall conclusions

We do not share the negativism of the reviewer regarding the severity factor. Obviously, the reviewer has worked for a long time in steam explosion and knows its phenomenology. But, at the same time, all the work in "steam explosion" lacks the unified thinking that we have attempted in this work. Further extension of our approach including the acid concentration in the severity parameter has been appended to these comments hoping that the reviewer begins to appreciate our generalized function and its usefulness.

We thank the reviewer for having acknowledged that our work proved the concept of fractionation at a level that nobody had tried before even it machinery was available for the last ten years and most groups working in the field had access to it.

Finally, nobody before us had made the link between aqueous and steam treatments. Workers in the field had failed to see the central unity of all these processes. Our attempt via a generalized severity parameter is a first step in this direction.

- Figures in pages 1331 -1335

The notations used $\log (R_0/\text{min.})$ and $\log R_0(\text{min.})$ are both clear enough and accepted ways of presenting data.

- Page B18 - line 1

The reviewer shows his colours with his inappropriate comment. He could have conducted the experiments himself several years ago! The machinery was there!

- Section C

We appreciate the explanation given on the 50% replacement of phenol by lignin in PF resins.

FINAL REMARK

One of the problems encountered by us in using other people's data and mapping it via our severity parameter is the lack of good material balances in most of the reported work, including the Forintek and New Zealand's data. The errors in the material balances, particularly when acids are used as impregnating agents, reflect in significant scattering and make any modelling extremely hazardous. Energies of activation and preexponential factors obtained by many authors are thus highly questionable.

REPLIES TO REVIEWER NO. 2

• General

- 1) The comments presented by the reviewer are appropriate.

The reviewer does not fully realize the enormous effort required to work at the pilot plant level. Our attempt was to provide a model to explain our data and compare it with existing information on other reactors and with biomass of different characteristics.

The general questions raised by the reviewer represent further steps in the refinement of the work which are being dealt with in the past few months.

The importance of the severity parameter is that it permits a rapid mapping of conditions regardless of biomass type and reactor used. Optimization of the conditions around a zone of "optimum fractionation" must be done at a later stage and will depend on the factors mentioned by the reviewer.

- 2) Units of R_0

R_0 has units of time.

We have corrected the inconsistencies in sections A and B of the report.

- 3) The mixture of S.I. and Imperial units is to be corrected in the revised text.
- 4) Remark on Section C is appropriate. Consumptions in 89 are not necessarily those of 82/83.

• Specific

- 1) The UdeS-SH process encompasses a series of treatments to fractionate the lignocellulosics.

When coupled to the STAKE process, the UdeS-SH approach consists of scavenging the lignin via caustic or a solvent (ethylene glycol/water is our favourite). This is done in a plug flow reactor in which we induce mechanical effects through homogenizing valves. Description of the process is adequately given in section A

It is also true that the reaction kinetics of TMV and TMAV process have been integrated into a single kinetic treatment.

- 2) Remark is OK but it is our policy to explicitly mention the names of the co-authors at the beginning of each section since different persons have participated to the research effort involved in each section.
- 3) From section A and B one comes to the conclusion that the maximum recovery of pentosans and lignin do not occur at the same R_0 . Thus a compromise (i.e. the optimum) has to be made to show the compatible recoveries of pentosans and lignin. This is done in sections A and B.
- 4) The introduction in section B involves some parts already covered in section A. This was done so to be able to have each section A and B as stand alone sections.
- 5) The cellulose yield is 100% of the initial cellulose up to $\log R_0 = 4.0$. This is clearly stated in paragraph 2 of the page B15.
- 6) Page B-16

Your comment is correct and that is the advantage of the R_0 concept.
- 7) Comment on the Figures is well taken.

FINAL REMARK

Your comments are constructive and well appreciated.

E. Chornet

Phenomenological Kinetics of Complex Systems. The Development of a Generalized Severity Parameter and its Application to Lignocellulosics Fractionation

by :

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Abstract

The rigorous modelling of complex reaction systems either homogeneous or heterogeneous is possible only when the sequence of all of the elementary steps is established. Few complex reactions have, however, a known and unambiguously determined set of elementary steps. Modelling of such complex systems is essentially phenomenological; thus, the kinetic parameters estimated lack mechanistic meaning and are functions of the ranges of experimental conditions used. Confronted with this situation, industrial applications of such complex reactions have adopted the use of severity factors which try to combine into a single parameter the effect of the different operational variables. The most known and universal severity parameter is the reaction ordinate H applied to pulping processes. In what follows we will focus on the application of the reaction ordinate to the case of biomass fractionation leading to hemicelluloses solubilization. We will propose a new generalized severity parameter which accounts for the acid catalyst effect on the extent of reaction. Despite the fact that the kinetics of complex systems are essentially phenomenological, we are presenting an approach derived from basic kinetic principles.



Introduction

It is widely accepted that a relatively limited number of reaction systems follow strictly an Arrhenius-type dependence of the rate constant versus temperature. Such systems are idealized examples which are well approximated by the collision or transition state theories. The reason for the limitation is that the energy probability factor " $\exp(-E/RT)$ " in the kinetic expressions is rigorously applicable only to processes for which the energy may be represented by two square terms, translational and rotational (Hinshelwood, 1940). The Arrhenius dependence followed by such ideal systems is not to be considered as a kinetic law but rather an empirical correlation which has universally been used as a landmark for the development of well established kinetic theories.

For complex systems in general, such as macromolecules, it is necessary to introduce a considerable number of vibrational energy terms which cause the probability factor for a given event to increase appreciably. The Arrhenius behaviour in such systems is indeed an approximation which is valid only for narrow ranges of experimental conditions where kinetic information can be correlated by means of rate expressions introducing nominal or pseudokinetic constants (i.e. preexponential factors and activation energies). These constants are obtained using sophisticated regression analyses and optimization techniques to statistically fit the data with minimum errors. However, the kinetic constants thus defined have three inherent limitations: a) they often lack mechanistic meaning ; b) the value of the constants vary from one experimental set to another and for different laboratories; and c) the use of the rate expressions beyond the narrow range in which the data has been correlated is not warranted and thus scaling-up beyond the experimental conditions used to obtain the data is unsound.

Frost and Pearson (1961) defined complex systems as those in which reactions do not take place via single collisions between reactant molecules, but via mechanisms involving several elementary processes or reactions steps. Although this is a good definition for systems in which the reactants are chemically identifiable individual molecules, it does not cover such complex substrates like biomass, coal, heavy oils, etc., in which the constitutive molecular units are arranged in three-dimensional matrices with numerous interlinkages (covalent bonds, hydrogen-bonds, etc.). These substrates are real complex systems and become almost

intractable by classical kinetics. In fact these systems are truly non-homogeneous complex reaction systems whose kinetic behaviour is not well described by simple formalisms. When we are referring to such systems the following points should be stressed:

1. There are numerous heterogeneous systems characterized by the presence of several physical phases and consequently the reactions taking place in such systems involve a large number of not well identified reaction (elementary or else) steps; hence the identification of a limiting step is a prerequisite in any attempt to model such systems.
2. There are also a significant number of macroscopically complex systems composed of different yet identifiable chemical species; we could distinguish two types of such systems which are both non-heterogeneous and, also, non-homogeneous:

- one-phase systems composed of polydisperse polymers whose variation in physico-chemical properties is such that we can essentially consider them as having a distribution of reactivities and/or kinetic parameters.

- microscopically heterogeneous systems composed of several distinct chemical families characterized by specific chemical linkages and special ultrastructures. As typical examples we can consider biomass (composed of cellulose, hemicelluloses, lignin, etc) and heavy oils (composed of parafins, olefins, aromatic, polyaromatic, polar and non-polar compounds with heteroatom linkages).

In these complex systems several chemical entities, i.e. the constitutive molecular or macromolecular compounds, are present together and undergo complex reaction sequences which transform them into products. The extent and the course of their transformation is ruled by a combination of the operating variables (usually temperature, pressure, time and catalyst concentration). The simplest approximation is that the course of the reaction for the entire system is the sum of the courses of the individual chemical entities which are considered to proceed independently from one another (i.e. no inter-reactions). Lin et al. (1984) working on thermal cracking of crude oils decided to model the behaviour of this complex system by dividing it into pseudo-components (subsystems) each following different first order kinetics. A linear combination of the pseudo-components represented the behaviour of the entire system while ignoring the possibility of interactions between the pseudo-components. Such systems of complex reactions have been treated in the literature in two ways:

a) The commonest way is to consider the system as being composed of discrete groups of species and reactions named "lumps". Within the lumps the individual species have similar reactivities and physical properties so that we are able to describe them by means of a unique set of kinetic parameters (i.e. frequency factor and activation energy). However such kinetic models usually lack any mechanistic meaning. Wei and Prater (1962), Kuo and Wei (1969), Wei and Kuo (1969), Hutchinson and Luss (1970), Luss and Hutchinson (1971), Golikeri and Luss (1972, 1974), Luss and Golikeri (1975) and Lee (1978) have studied extensively such complex reaction systems. In modelling such reaction systems one cannot use the unit "mol" as a measure of concentration; such a unit is difficult to be monitored due to the near impossibility to measure or even identify the chemical species reacting or produced. Instead mass units expressing usually the conversion of a reactant or the yield of a product are extensively used in the literature.

b) The alternative approach to model the reactions complex systems is to consider that they follow a continuous distribution of reactions which lead to the disappearance of reactants and the appearance of products via a sequence of often unknown chemical pathways. Aris and Gavalas (1966) described first this method. Overend and Chornet (1990), in modelling heavy oil cracking, made the assumption that the first order reaction rate constant is a function of time and showed that, if $k=k_0 \cdot t^{\gamma-1}$, the activation energy can be represented by a distribution given by the Kohlrausch function $\Phi(t)$ previously described by Plonka (1986); the shape of this function depends on values of the parameter γ .

Biomass systems (i.e. lignocellulosics, peat, starchy materials, cellular structures, e.t.c.) are a large and special category of complex systems in which the predominant chemical linkages are susceptible to hydrolysis reactions. Focusing in lignocellulosics as a prototype complex system we noticed that modelling of the hydrolysis has traditionally been approached with the following three assumptions:

- the principles and laws applicable to homogeneous systems have been universally used to model the behaviour of the hydrolysis of the heterogeneous lignocellulosic material in steam/aqueous treatments;
- the constitutive subsystems in lignocellulosics (i.e. lignin, hemicelluloses, cellulose and extractives) do not interact during hydrolysis;

- each individual subsystem is treated as being predominantly characterized by a distinct chemical linkage which is typically an ether bond (C-O-C). Such a simplification leads to a simple kinetic expression representing the rupture of such bonds.

Analysis of the above assumptions leads to the following conclusions:

- the first assumption allows the use of the rate expressions developed for the homogeneous systems and which are clearly based on Arrhenius-type behaviour. This is indeed a great simplification of the reacting system since matrix effects limiting heat and mass transfer are neglected. These matrix effects may force local conditions quite different from those present in the bulk of the reacting medium;
- the second assumption assures a linear behaviour. Hence, the total conversion becomes the sum of the conversions of the individual subsystems. There is, however, plenty of evidence that inter-subsystems reactions do take place; besides, reactions between the substrate and the products are well documented. Thus, McKibbins et al. (1962) proved the existence of condensation reactions between formed anhydrosugars and the substrate during acid hydrolysis of glucose; Brennan et al. (1986) and Abatzoglou et al. (1990) outlined the importance of condensation reactions, whose exact nature is still unknown, during the acid hydrolysis of hardwoods; Joseleau and Kesraoui (1987) proved that new lignin-carbohydrates bonds are created during wood pulping suggesting that such inter-subsystems reactions are indeed present;
- the third assumption above considered is reflected by constant kinetic parameters for each particular subsystem. Ederer et al. (1981) tried to model the acid catalyzed hydrolytic depolymerization of dextran and showed that, even if dextran has a rather regular molecular structure, the formation of small molecules (i.e. monomers) during hydrolysis is higher than expected, when a statistical degradation pathway is assumed; thus, he concluded that the 'individual' degradation rate constants of the different polymer bonds are dependent on the degree of polymerization and the location in the polymer chain. Torres et al. (1985) showed that, for the hydrolysis of cellulose, a regular and uniform macromolecule, each author working in the field obtains, through experimentation, a new set of kinetic parameters; the key point, however, is that in all cases the energies of activation are substantially higher than known values for the acid catalyzed rupture of β -glucosidic bonds in homogeneous systems.

The above discussions have led us to consider that in a complex system such as lignocellulosic biomass, the concepts of formal kinetics do not match the complexity of the system. As well the interrelationships and relative weight of the operating variables in the rate expression cannot be expressed in terms of the conventionally defined Arrhenius parameters. Instead we can say that the frequency factor and the activation energy representing the Arrhenius expression are not constant during the reaction; however their variations with extent of reaction are not known and assumptions are needed to model such reaction behaviour.

The different possibilities proposed so far in the literature assume that the frequency factors do vary but slightly and consequently could be considered constant while activation energies vary significantly following some deterministic laws. The most frequently used assumptions to express these activation energies variations are as follows:

1. the activation energy has a constant value and consequently is independent of the extent of reaction and does not change with time.
2. the "lumped" system approach: each particular chemical family or species is characterized by a single constant activation energy not varying with time either; however the entire reaction system is not expressed by a single combination of frequency factor-activation energy but rather by a set of such combinations reflecting the contribution of each family to the overall reaction.
3. the "continuous distribution of activation energies" approach in which we can distinguish two categories:

3a. the complex reaction system is composed of chemical species (belonging to the same or to different chemical families) whose activation energies follow a continuous distribution. Anthony and Howard (1976) and Ko et al. (1988) have proposed a Gauss distribution to simulate the reactions taking place in pyrolytic systems.

3b. the complex reaction system is composed of chemical species in such a way that the rate constant characterizing their reactions is a function of time. Overend and Chornet (1990) used this assumption to model the heavy oil cracking reactions as already mentioned.

Efforts to develop severity parameters regrouping the operating variables have been made in the past. Most of these efforts have considered temperature and time as the variables most likely to influence the conversion of a given reactant. Thus the severity parameter will be a function of these two variables and will serve to predict the extent of conversion or a product yield. Geniesse and Reuter (1930) used the

following time-temperature index (S.I.) to model the cracking of oils:
" $S.I. = 2 \cdot ((T-480)/17) \cdot t$ " ; Powell (1950) showed that for simple as well as for many complex reactions a plot of relative product concentration or the extent of reaction as a function of $\log(t)$ provides a pattern whose shape depends only on the type of reaction and a few dimensionless parameters; Overend and Chornet (1987) explained the development and application of the reaction ordinate " $R_o = \exp((T-100)/14.75) \cdot t$ " to map the destructuring, the disaggregation and the depolymerization of lignocellulosics. The R_o concept provides a zonal indication of the predominant reactions taking place in lignocellulosics.

Since acid and base catalysts are important in hydrolysis their role in a given reaction should be accounted in the severity parameter. Successful efforts in the direction of combining the severity parameter R_o and acidity $[H^+]$ into an extended severity parameter, $R' = R_o \cdot [H^+]$, have been made by Chum et al. (1990) in their studies concerning the acid catalyzed organosolv delignification of lignocellulosics.

Given the fact that the severity concepts are so far empirically motivated we have felt that a general approach is necessary and that a formal link with basic kinetics should be made in order to unify the modelling of simple and complex reacting systems.

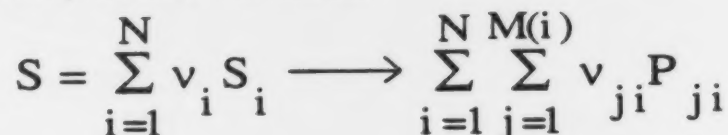
In what follows we present a systematic approach aimed at the definition of a generalized reaction ordinate including catalytic effects. An application of the approach to the solubilization of hemicelluloses following aqueous/steam treatments of lignocellulosics is also presented.

To derive a more generalized reaction ordinate we have used both the "lumped" and the "continuous distribution of activation energies" approaches as described herein.

Mathematical formalism

1. The "Lumped" System approach

A complex reaction system (S) composed of N individual subsystems (S_i) could be represented as follows:



where:

v_i, v_{ji} are the stoichiometry coefficients
 P_{ji} are the final products and
 $M(i)$ are the number of final products derived from each particular subsystem

In such systems, the arrow symbolizes a complex and rather unknown reaction pathway, usually involving many intermediate steps and products. In short "the transfer function" is unknown. This implies that the only acceptable way to monitor the extent of reaction is the measurement of the disappearance of each subsystem, since the final or intermediate products P_{ji} are in many cases not necessarily known.

The conversion, f , of the entire system is given by the following expression:

$$\frac{df}{dt} = \sum_i x_i \left(\frac{df_i}{dt} \right) \quad (1)$$

where: $f = 1 - \frac{S}{S_0}$ and $f_i = 1 - \frac{S_i}{S_{i0}}$

i = specific subsystem i

x_i = weight or molar fraction of i

Equation (1) allows us to monitor the whole reaction by means of the total conversion or through the conversion of each individual subsystem.

In our case study (hemicelluloses in the fiber $\longrightarrow$ hemicelluloses in solution) we will consider the hemicelluloses as a particular subsystem within a larger lignocellulosic system. The "phenomenological rate expression is:

$$\frac{df_i}{dt} = \frac{v_i}{S_i^0} k [T, \text{Catalyst}] F[S_i^0(1-f_i)] \quad (2)$$

where:

k is the reaction rate constant which is a function of temperature and catalyst concentration and

F is an unknown function of the reactants (unknown because we know little or nothing about the real reaction mechanism).

One can distinguish two situations:

a) the uncatalyzed reaction

In this case equation (2) transforms into :

$$\frac{df_i}{dt} = \frac{v_i}{S_i^0} k [T] F[S_i^0(1-f_i)] \quad (3)$$

If we let k[T] follow Arrhenius dependence, we obtain:

$$\frac{S_i^0}{F[S_i^0(1-f_i)]} \left(\frac{df_i}{dt} \right) = v_i k_0 \exp \left\{ - \frac{E_i}{RT} \right\} \quad (4)$$

and taking logarithms:

$$\ln \left\{ \frac{S_i^0}{F[S_i^0(1-f_i)]} \left(\frac{df_i}{dt} \right) \right\} = \ln \{ v_i k_0 \} - \frac{E_i}{RT} \quad (5)$$

If we make a Taylor series expansion of the temperature function we will

linearize the expression with respect to the temperature. The expansion of for any given function F is :

$$\Phi L(T) \equiv \Phi L(T_{ref}) + \left(\frac{d\Phi L}{dT} \right)_{T_{ref}} (T - T_{ref})$$

After the expansion , equation (5) becomes :

$$\ln \left\{ \frac{S_i^0}{F[S_i^0(1-f_i)]} \left(\frac{df_i}{dt} \right) \right\} = \ln \{ v_i k_0 \} - \frac{E_i}{RT_{ref}} + \frac{T - T_{ref}}{\frac{RT_{ref}^2}{E_i}} \quad (6)$$

If one lets $\frac{RT_{ref}^2}{E_i} = \omega$, and takes the antilogarithmic function while separating variables, equation (6) becomes:

$$\int_0^{f_R} \frac{S_i^0}{F[S_i^0(1-f_i)]} df_i = \int_0^{t_R} \left[v_i k_0 \exp \left\{ - \frac{E_i}{RT_{ref}} \right\} \right] \cdot \left[\exp \left\{ \frac{T - T_{ref}}{\omega} \right\} \right] dt \quad (7)$$

which can be simplified as follows:

$$\int_0^{f_R} \frac{S_i^0}{F[S_i^0(1-f_i)]} df_i = \left\{ v_i k_{T_{ref}} \right\} R_0 \quad (8)$$

where: $k_{T_{ref}} = k_0 \exp \left\{ - \frac{E_i}{RT_{ref}} \right\}$ $R_0 = \int_0^{t_R} \exp \left\{ \frac{T - T_{ref}}{\omega} \right\} dt$

Equation (8) indicates that the left hand side, which is dependent on conversion only, is an exclusive function of R_0 , the reaction ordinate, hitherto defined empirically. The problem is that function F is unknown and consequently its integration is not possible.

Nevertheless, Powell's observation that "the plot of reaction extent vs log(t) produces a curve whose form depends only upon the type of reaction

and possibly some dimensionless parameters* is indeed explained by Equation (8).

b) the catalyzed reaction

In this case Equation (2) is the basic expression from where the rate expression should be derived. The question is: how does the catalyst influences the reaction system?

Three possibilities prevail:

- (i) if the catalyst lowers the activation energy barrier then E_i will be affected;
- (ii) if the catalyst acts upon the structure, the accessibility or the orientation of reactants and intermediates, therefore influencing the entropy of the system, the parametre k_0 will be directly affected;
- (iii) both k_0 and E_i are affected when the catalyst acts upon the activation energy as well as on the orientation, the accessibility and the structure of reactants.

If we represent by X the catalyst concentration we can introduce the catalyst effect as follows:

$$E_i^* = E_i - nX \quad (9-1)$$

or

$$E_i^* = E_i - n \log(X) \quad (9-2)$$

Alternatively, if the preexponential factor is affected then:

$$k_o^* = k_o \exp(mX) \quad (10-1)$$

or

$$k_o^* = k_o \exp\{m \log(X)\} \quad (10-2)$$

Comparing Equations (9-1) and (9-2) with Equations (10-1) and (10-2), both sets of expressions lead to similar results after a series expansion. From Equations (9-1) and (10-1), Equation (2) is transformed into:

$$\ln \left\{ \frac{S_i^0}{F[S_i^0(1-f_i)]} \left(\frac{df_i}{dt} \right) \right\} = \ln \{ v_i k_0 \} + mX - \frac{E_i - nX}{RT} \quad (11)$$

A Taylor series expansion of expression $\left[mX - \frac{E_i - nX}{RT} \right]$ around (X_{ref}, T_{ref}) will give us a linearization with respect to the catalyst concentration and the temperature. The general expression for this expansion is:

$$\Phi L[X, T] = \Phi L[X_{ref}, T_{ref}] + \left(\frac{\partial \Phi L}{\partial X} \right)_{T_{ref}, X_{ref}} (X - X_{ref}) + \left(\frac{\partial \Phi L}{\partial T} \right)_{T_{ref}, X_{ref}} (T - T_{ref})$$

which, once applied to Equation (11) gives:

$$\ln \left\{ \frac{S_i^0}{F[S_i^0(1-f_i)]} \left(\frac{df_i}{dt} \right) \right\} = \ln \{ v_i k_0 \} + \left[mX_{ref} - \frac{E_i - nX_{ref}}{RT_{ref}} \right] - \left(m - \frac{n}{RT_{ref}} \right) (X - X_{ref}) + \frac{E_i - nX_{ref}}{RT_{ref}^2} (T - T_{ref}) \quad (12)$$

Taking the antilogarithmic function and defining ω' and λ as:

$$\omega' = \frac{RT_{ref}^2}{E_i - nX_{ref}} \quad (12-1)$$

$$\lambda = \left[mX_{ref} - \frac{nX_{ref}}{T_{ref}} \right]^{-1} \quad (12-2)$$

Equation (12) becomes:

$$\int_0^{f_r} \left\{ \frac{S_i^0}{F[S_i^0(1-f_i)]} df_i \right\} = [v_i k_0 \exp(m X_{ref}) \exp\left(\frac{E_i - n X_{ref}}{RT_{ref}}\right)] \int_0^{t_r} \exp\left\{\frac{X - X_{ref}}{\lambda X_{ref}}\right\} \exp\left\{\frac{T - T_{ref}}{\omega}\right\} dt \quad (13)$$

if we define R_{OH} as:

$$R_{OH} = \int_0^{t_r} \exp\left\{\frac{X - X_{ref}}{\lambda X_{ref}}\right\} \exp\left\{\frac{T - T_{ref}}{\omega}\right\} dt \quad (14)$$

we obtain:

$$\int_0^{f_r} \left\{ \frac{S_i^0}{F[S_i^0(1-f_i)]} df_i \right\} = [v_i k_0 \exp(m X_{ref}) \exp\left(\frac{E_i - n X_{ref}}{RT_{ref}}\right)] R_{OH} \quad (15)$$

Equation (15) indicates that the left hand side, which is totally dependent on conversion, is an exclusive function of R_{OH} . R_{OH} is then a new reaction ordinate extended to cover catalyzed systems. If, instead of Equations (9-1) and (10-1), we use Equations (9-2) and (10-2) respectively, the definition of the new reaction ordinate should not change; the proportionality factor multiplying R_{OH} in Equation (15) will integrate the additional constants.

If the reaction is isothermal we will have the following expressions for R_0 and R_{OH} respectively:

$$R_0 = \exp\left\{\frac{T - T_{ref}}{\omega}\right\} t_r \quad (16-1)$$

$$R_{OH} = \exp\left\{\frac{X - X_{ref}}{\lambda X_{ref}}\right\} \exp\left\{\frac{T - T_{ref}}{\omega}\right\} t_r \quad (16-2)$$

where, t_r is the total reaction time.

2. The Continuous Distribution of Activation Energies approach

If we make the assumption that our complex reaction subsystem, described previously, is characterized by an infinite number of reaction steps for which the activation energies are not constant but evolve with time in such a manner that their time distribution obeys to the Kohlrausch function we can write that :

$$k = k_0 \exp\left\{-\frac{E}{RT}\right\} t_r^{\gamma-1} \quad (17)$$

where : $0 < \gamma \leq 1$

If we use this expression in our calculation we can easily show that the generalized severity parameters obtained for both the non-catalytic and catalytic case can be described by Equations (18) and (19) respectively:

$$R_0 = \exp\left\{\frac{T - T_{ref}}{\omega}\right\} \frac{t}{\gamma} \quad (18)$$

$$R_{0H} = \exp\left\{\frac{X - X_{ref}}{\lambda X_{ref}}\right\} \exp\left\{\frac{T - T_{ref}}{\omega}\right\} \frac{t}{\gamma} \quad (19)$$



Application of the model to four case studies

Experimental Methods and Results

Corn stalks from the St. Hyacinthe region (Quebec, Canada) and Alfa (*Stipa Tenacissima*) obtained from half-desert regions in Algeria have been used, as feedstocks representatives of graminæ plants, to study and optimize the solubilization of hemicelluloses, by means of an aqueous/steam treatment described by Abatzoglou et al., (1990) and Belkacemi, (1990). Since our aim was to develop a general method to model the hydrolytic solubilization of hemicelluloses, we also considered results from the literature. In Table 2 we summarize the operational conditions and ranges of results obtained during our work with corn stalks and alfa as well as by Springer et al., (1963), and Maloney et al., (1986), who worked on *Populus tremuloides* and *Betula papyrifera* respectively. All four sets of results will be used to prove the usefulness of the generalized reaction ordinate and estimate the two characteristic empirical parameters.

23 experimental points were used for the corn stalks, 24 for the Alfa, 47 for the Betula and 132 for the Populus.

The process development unit (PDU) used is presented in Figure 1. The experimental procedure consists of :

- 1) an aqueous medium consistency suspension (8-10%w/w) of finely ground substrate is fed to a reservoir (T-2), wherein is recirculated at 1 m/s by means of a simple positive displacement pump (P-5) in order to homogenize the suspension and facilitate its flow;
- 2) one tenth (or about) of the recirculated suspension is continuously withdrawn and pumped to a steam-slurry mixer (V-12), specially designed for the admission of open steam, to heat the slurry almost instantaneously up to the desired reaction temperature;
- 3) the heated slurry is forced through a second homogenizing valve (V-26) under pressure differentials as high as 30 MPa;
- 4) an appropriate amount of preheated acid solution (5% H₂SO₄ w/w) can be injected into the slurry via pump P-30, if an acid catalyzed hydrolysis experiment is desired;
- 5) the slurry (acidified or not) is flown through an isothermal tubular reactor (R-32);
- 6) after a preestablished residence time in the tubular reactor the reacted slurry is neutralized just at the reactor outlet by the on-line injection of a base (NaOH) solution (pump P-35), then flashed at barometric pressure to separate the slurry from the steam (vessel T-32);

7) the flashed vapor containing some volatiles is then sent to a total condenser (C-34) while the treated slurry phase is also recovered for subsequent separation, via a filter centrifuge, and analysis.

In Table 1 we show the composition of the initial substrates, whose determination has been performed following the ANSI/ASTM and TAPPI methods for biomass. A complete description of the methods used is presented by Abatzoglou, (1989), and Belkacemi, (1990). In Figure 2 we present a thorough description of the protocol used to analyze the products of the aqueous/steam treatment. A key analytical determination is the hemicelluloses remaining (unconverted) in the final solid residue. Through material balances, the sum of the unconverted hemicelluloses and the solubilized fraction should equal the amount of hemicelluloses, present in the initial biomass; At low severity treatments, where no significant carbohydrate degradation reactions occur, the material balances had excellent closures whereas at high severities the rapid degradation of the solubilized hemicelluloses leads to dehydrated and acidic products whose quantification could not be conclusively done. Thus we based our kinetic analysis on the residual hemicelluloses present in the treated fiber.

Choices for X_{ref} and T_{ref}

The choice of X_{ref} forces a decision on the units to use for the catalyst concentration. In general the units will be decided by the nature of the complex system under study. Thus, units such as weight, moles or even number of sites of catalyst per unit weight of substrate are all acceptable. In the present paper we will use weight units (g of catalyst/g of substrate). Thus X becomes dimensionless.

(a) The T_{ref}

Its choice will depend on the particular system being studied. In the present case, i.e. the hemicelluloses solubilization via hydrolysis, the reference temperature is chosen as a base temperature where little or no reaction occurs during the time period normally considered for the reaction. Even if the literature shows that the hydrolytic reactions of complex carbohydrates as hemicelluloses are slow at 100°C we have preferred to choose 70°C as T_{ref} . This choice is motivated by the satisfactory results obtained during optimization steps to be described later.

One can wonder why T_{ref} is not chosen in the middle of the experimental temperature range. The answer lies in that there is no specific reason to do so and that a choice of T_{ref} outside the experimental range allows to refer to a common observational point from where the complex system behaves as an exponential function of temperature insofar the kinetic conversion term is concerned.

(b) The X_{ref}

We have decided to maintain the criterion of the choice of a catalytic concentration at which no catalytic (i.e. hydrolytic) action occurs at any significant level. Ullah et al. (1984) reported that, in corn stover acid hydrolysis at 175°C, no catalyzed hydrolysis was observed below an acid loading of 0.017 g of acid/g of substrate. This meant that the polyelectrolyte behaviour of the lignocellulosic matrix is able to neutralize the acidity up to that level. It is then clear that any value below 0.017 g/g will be a "safe" choice for X_{ref} . To simplify calculations, our choice has been $X_{ref} = 0.01$ g/g.

The question related to the above choices for T_{ref} and X_{ref} is whether the residual terms in the series expansion, undertaken to linearize the conversion function versus the operating variables, will become important since the reference points are well outside the experimental range. Our answer is that the reference points chosen are so far away from the experimental region that the errors involved are equal for all of the experimental points. Corrections to the series expansion can be introduced in the optimization sequence in a manner similar to the method detailed by Overend and Chornet (1990) who introduced the second derivative on a correction to $\log(R_0)$ in order to improve the correlation coefficient during the regression analysis to fit their model to the data.

The optimization of λ , ω' and γ

Equation (15) could be written in the following way:

$$\int_0^{f_{if}} \left\{ \frac{S_i^0}{F[S_i^0(1-f_i)]} \right\} df_i = K \cdot R_{0H} \quad (20)$$

where,
$$K = v_i k_0 \exp\{mX_{ref}\} \exp\left\{\frac{E_i - nX_{ref}}{RT_{ref}}\right\} \quad (21)$$

and R_{0H} has been defined in Equation (16).

Since function F is unknown, we have no means of conducting a non-linear regression analysis to obtain the optimum λ and ω' values in the case of the "Lumped" System assumption or the optimum λ , ω and γ in the case of the Continuous Distribution of Activation Energies assumption. Thus, we decided to make the hypothesis that our reaction is either of 1st or 2nd order with respect to the reactant substrate (i.e. the hemicelluloses present in the fiber). In these two cases the development of Equation (20) leads to:

a) 1st order
$$-\ln(1-f_{if}) = K \cdot R_{0H} \Rightarrow f_{if} = 1 - \exp\{-K \cdot R_{0H}\} \quad (22)$$

b) 2nd order
$$\frac{f_{if}}{1-f_{if}} = K \cdot R_{0H} \Rightarrow f_{if} = \frac{K \cdot R_{0H}}{1 + K \cdot R_{0H}} \quad (23)$$

A non-linear regression analysis program based on the method of "the steepest descent" has been used to estimate the optimum parameters in

both cases and for all four sets of experimental data available. The errors in the fitting encountered for the 2nd order case were twofold higher than those in the 1st order case. This is in good agreement with literature where most of the studies are based on 1st order kinetics for the hemicelluloses solubilization. More details about the optimization program are available from Belkacemi (1990).

The results of the optimization for 1st order kinetics, are presented in Tables 3 ("Lumped" System model) and 4 (Continuous Distribution of Activation Energies model). Using these values, we have fitted the models to the experimental data. The results of this fitting are presented in Figures 3,4,5,6,7,8,9,10 for the four different data sets considered.

Results and Discussion

The "Lumped" System approach in which we have considered our reacting system as being composed of N homogeneous subsystems led, in terms of fitting errors, to better results when compared with the "Continuous Distribution of Activation Energies" approach. Although this conclusion is statistically sustained by a Fischer test for three of the biomasses studied it could not be extended to the fourth data set available. However, both approaches proved well performing to fit the extent of the hydrolytic solubilization of hemicelluloses of the four different lignocellulosic biomasses herein considered.

The results of the estimation of the two parameters ω' and λ ("Lumped" System approach) as well as ω' , λ and γ (Continuous Distribution of Activation Energies approach) by means of a non-linear regression analysis method are presented in Tables 5 and 6 respectively. These results combined with an appropriate statistical analysis of the models proposed showed the following:

1. "Lumped" System approach

- The ω' optimal value is similar for all four biomasses; in fact the differences encountered are less than $\pm 10\%$ from a central value of 9.3. This is what should have been expected since this parameter is associated with the glucosidic bond strength (and consequently with its activation energy for the hydrolysis). If we do accept that ω' is given by Equation (12-1) and that the term nX_{ref} is negligible (which is a good assumption) then the activation energy corresponding to $\omega'=9.3$ is $E=105\,085$ J/mol. This value is in accord with the activation energy of the homogeneous glucosidic bond hydrolysis given in literature (Belkacemi, 1990).

- The optimal value of λ is different for each particular biomass; we have to keep in mind that this parameter is associated with the acid catalytic effect. If we make the hypothesis that the activation energy is equally affected by the acid for all four biomasses, because the glucosidic bonds have similar strengths, we must conclude that the main reason for these differences is that the structural effects are different for each type of biomass and consequently the acid effect does not give the same results. In other words (see Equations (9-(1,2) and 10-(1,2)) the parameter m

should be similar for all biomasses while n should not.

- Using the optimized ω' , λ and K values in Equation (21) we have backcalculated k_0 values corresponding to the frequency factor in the Arrhenius law. The results showed that k_0 takes values within the range of $1.5E-20$ and $7.0E-24 \text{ min}^{-1}$. These seem to be low values when compared with the ones proposed in the literature for the heterogeneous acid hydrolysis of the hemicelluloses; we have, however, to mention that the activation energies available in the literature are higher than those obtained in this work and that there is a compensation effect between these two parameters (k_0 and E) as showed by Belkacemi (1990)

- The previous discussion on ω' and λ and the conclusions hereby drawn apply only if the model proposed is statistically "robust". This means that the mutual sensitivity of ω' and λ is such that errors normally distributed around a central value of ω' do not lead to λ changes higher than the order of magnitude of the normal errors. To investigate the latter we have proceeded to a series of new optimizations in which ω' takes values within a range of $\pm 10\%$ around the mean ω' and new λ optima are estimated, simultaneously with the proportionality factor K . In Figure 11 we present the results of these optimizations. In fact we see that variations of the ω' within the $\pm 10\%$ region lead to $\pm 30\%$ variations for the λ . Given the fact that the differences observed between the λ values for the different biomasses are much higher than this 30% theoretically estimated we can claim that our model is consistent and statistically "robust" for the applications tested.

Moreover, a normal probability plot of residuals (as proposed by Daniel, 1959) depicted in Figure 12 shows that the statistically important parameters for our model are the ω' (of high importance) and λ (of lesser importance) while all other combinations (K , $K\lambda$, $K\omega'$, $\lambda\omega'$, $K\lambda\omega'$) are not statistically considerable. According to this method a factorial grid is used for the three parameters at 2 levels (2³ combinations). In our case the 3 parameters are K , ω' and λ and the two levels $\pm 10\%$ and -10% away from the central optimized values. One biomass (*Betula pap.*) is used for the herein reported test but all other biomasses gave similar results.

2. The Continuous Distribution of Activation Energies approach

- Regarding the ω' optimal values we can draw the same conclusion as previously. In fact for the four biomasses the ω' varies between 10.0 and 13.5. We observe however a larger spread of values and the standard deviation from the mean value is of about 15%.
- The optimized λ values follow the same pattern and we can say that the differences observed are due to the physico-chemical behaviour of each particular reaction system.
- According to our assumptions the complex reaction system is represented by a continuous distribution of activation energies obeying to the Kohlrausch function and having a mean activation energy between 10.0 and 13.5 and γ taking values from the range included between 0.71 and 0.8 (0.745 $\pm$ 8%).
- More work is under way to verify statistically the robustness of this model.

Conclusions

The "Lumped" System approach is essentially based on the assumption that our system is behaving as being homogeneous while the Continuous Distribution of Activation Energies approach considers that $k=k(t)$ or in other words that the reaction rate constant is a function of time or extent of reaction.

Both phenomenological models developed, based upon the severity factor concept, predicts satisfactorily the acid catalyzed solubilization of hemicelluloses of four different lignocellulosic biomasses. The optimization work conducted shows that universal values can be used for ω' and γ while λ values depend on the physico-chemical characteristics of each particular substrate.

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Nomenclature

$\bar{E}$ = mean activation energy

E_i = activation energy of the uncatalyzed subsystem i

E_i^* = activation energy of the catalyzed subsystem i

$F[]$ = a function

f = conversion of the entire complex system

f_i = conversion of the subsystem i

f_{if} = final conversion of the subsystem i

i, j = number indexes

k = reaction rate constant

K = a constant defined in the text

k_0 = frequency factor in Arrhenius law (non catalytic case)

k_0^* = frequency factor in Arrhenius law (catalytic case)

m, m', n = parameters expressing the catalyst effect in
activation energy and entropy

P_{ji} = final products of subsystem i

R = gas constant

R_0 = the severity factor for the non catalytic case (min)

R_{0H} = the severity factor for the catalytic case (min)

S = complex system and concentration of initial substrate

S_i = subsystem i and concentration of reactive substrate i at time t

s_i^0 = initial concentration of reactive substrate i

T = temperature (°C)

T_{ref} = reference (or base) temperature (°C)

t = time (min)

t_R = reaction time (min)

Greek symbols

γ = parameter defining the shape of the Kohlrausch function

λ = parameter expressing the acid catalyst role in conversion of the system

v_i, v_{ji} = stoichiometric factors

τ_0 = parameter of the Kohlrausch function defined in the text

$\Phi(t)$ = the Kohlrausch function

$\Phi L[]$ = a function to be linearized

X = acid loading (g of acid / g of dry biomass)

X_{ref} = reference (or base) acid loading (g of acid / g of dry biomass)

ω = parameter expressing the temperature role in conversion of the uncatalyzed reaction system

ω' = parameter expressing the temperature role in conversion of the catalyzed reaction system

TABLE 1
Composition of the Biomass Materials Used in
this Study
All the Results are expressed in % w/w of dry
Original Material

Compos. Biomass Substrates	Extractives		Ash	Lignin	Hemicel.	Cellulose
	Eth./Tol.	Water				
Corn stalks	7.7	10.7	7.1	16.4	29.2	29.0
Stipa tenacissima	2.0	5.0	3.1	18.0	34.0	37.0

TABLE 2
Experimental Conditions

Biomass	Reactor	Temperature(°C)	Time(min)	Acid(%w/w)	Hemicelluloses initial - final	References
Corn Stalks	Isothermal Tubular	120-240	0.6-5.0	0.0-0.2	100 - 10	Belkacemi (1990)
Stipa tenacissima	Isothermal Tubular	120-240	0.6-5.0	0.0-0.1	100 - 20	Belkacemi (1990)
Populus tremuloides	Isothermal Batch	100-150	0-10	0.5-0.2	100 - 4	Springer et al. (1963)
Betula papyrifera	Isothermal Batch	100-150	0-1000	0.4-1.8	100 - 0	Maloney et al. (1986)

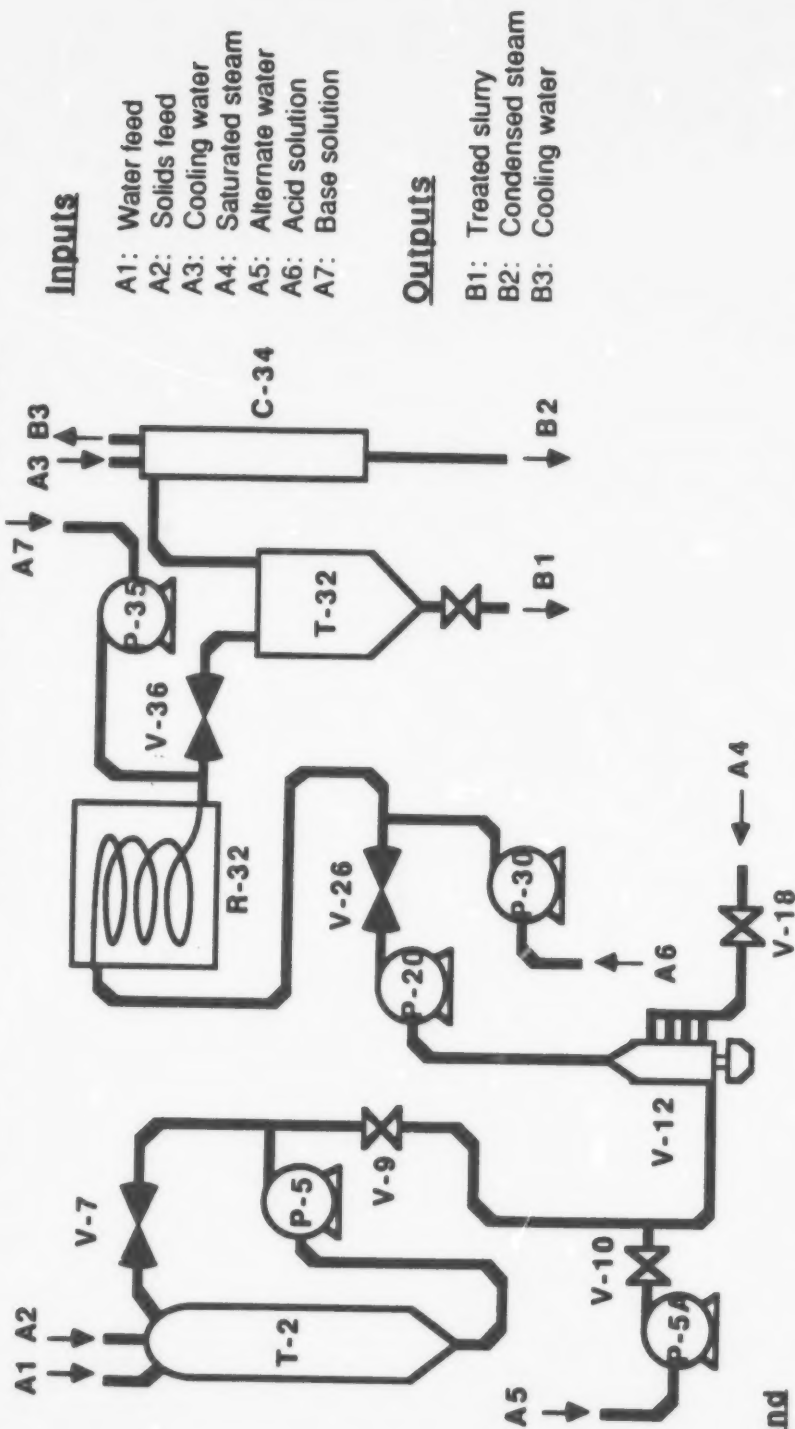
TABLE 3
The Optimization Results for the
"Lumped" System Assumption

Biomass	ω_{optimum}	λ_{optimum}	K_{optimum}	σ_{n-1}	References
Corn Stalk	9.6	52.6	0.2E-6	0.11	Belkacemi (1990)
Alfa	9.4	28.6	0.7E-7	0.17	Belkacemi (1990)
Populus Tremuloides	8.4	125.0	1.6E-4	0.08	Springer et al.(1963)
Betula Papyrifera	9.7	90.9	3.5E-5	0.04	Maloney et al.(1986)

TABLE 4
The Optimization Results for the
Continuous Distribution of Activation Energies Assumption

Biomass	ω_{optimum}	λ_{optimum}	γ_{optimum}	K_{optimum}	σ_{n-1}	References
Corn Stalk	10.0	58.8	0.74	0.7E-7	0.18	Belkacemi, 1990
Alfa	10.3	21.7	0.73	0.5E-7	0.16	Belkacemi, 1990
Populus tremuloides	12.2	166.7	0.71	1.0E-3	0.09	Springer et al., 1963
Betula papyrifera	13.5	100.0	0.80	0.2E-3	0.07	Maloney et al., 1986

Figure 1
The Process Development Unit Flowsheet



Legend

- | | | | | | |
|-------|------------------------------|-------|---------------------------------------|-------|-------------------------------|
| T-2: | Feed reservoir | P-20: | Hot slurry piston pump | V-36: | Homogenization valve (High T) |
| P-5: | Recirculation piston pump | V-26: | Homogenization valve (High T) | P-35: | Metering pump |
| V-7: | Homogenization valve (Low T) | P-30: | Metering pump | T-32: | Product discharge vessel |
| P-5A: | Metering piston pump | R-32: | Thermostated tubular reactor module | C-34: | Vapor condenser |
| V-12: | Steam-slurry mixer | V-18: | PID control valve for steam injection | | |

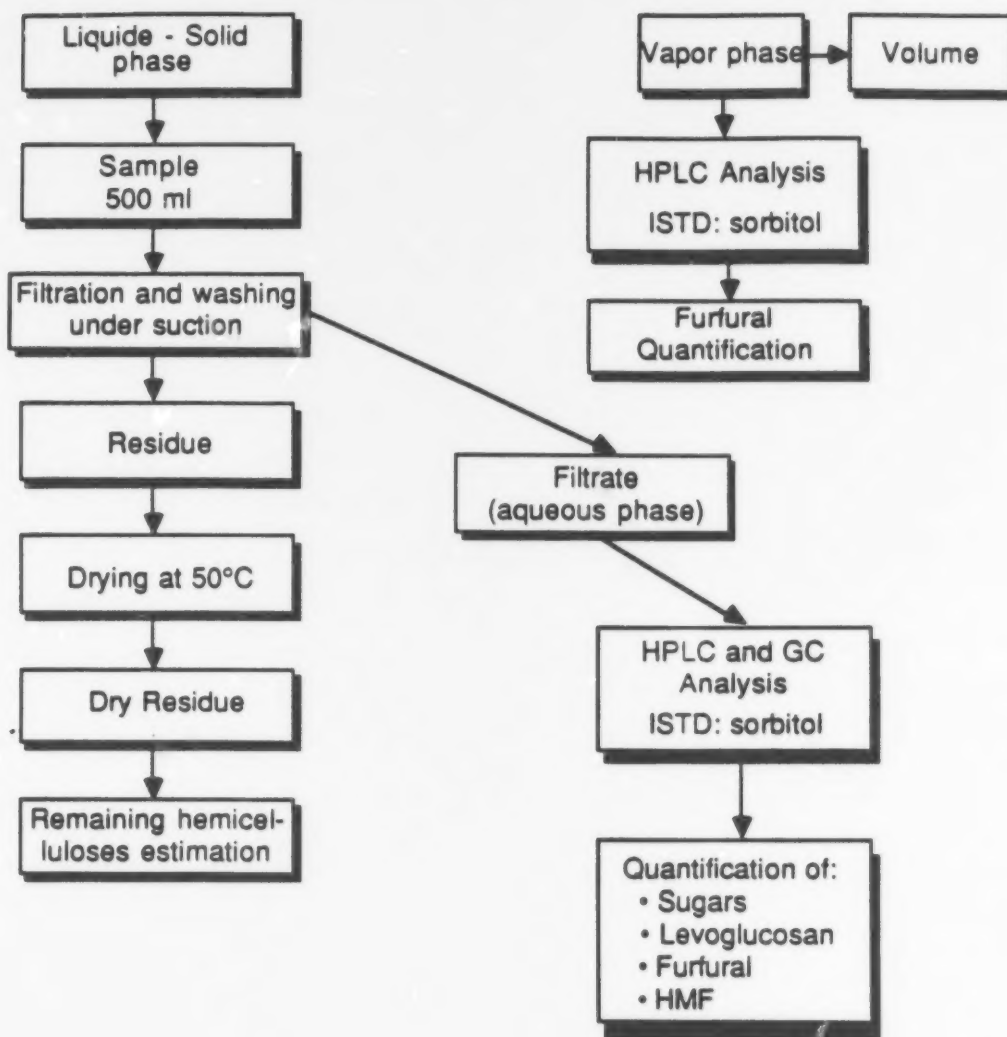
Inputs

- A1: Water feed
- A2: Solids feed
- A3: Cooling water
- A4: Saturated steam
- A5: Alternate water
- A6: Acid solution
- A7: Base solution

Outputs

- B1: Treated slurry
- B2: Condensed steam
- B3: Cooling water

FIGURE 2
The Analytical Protocol



Note: All of the results are reported to the initial volume.

FIGURE 3
Data and Model for Corn stalks Hydrolysis
("Lumped" System Case)

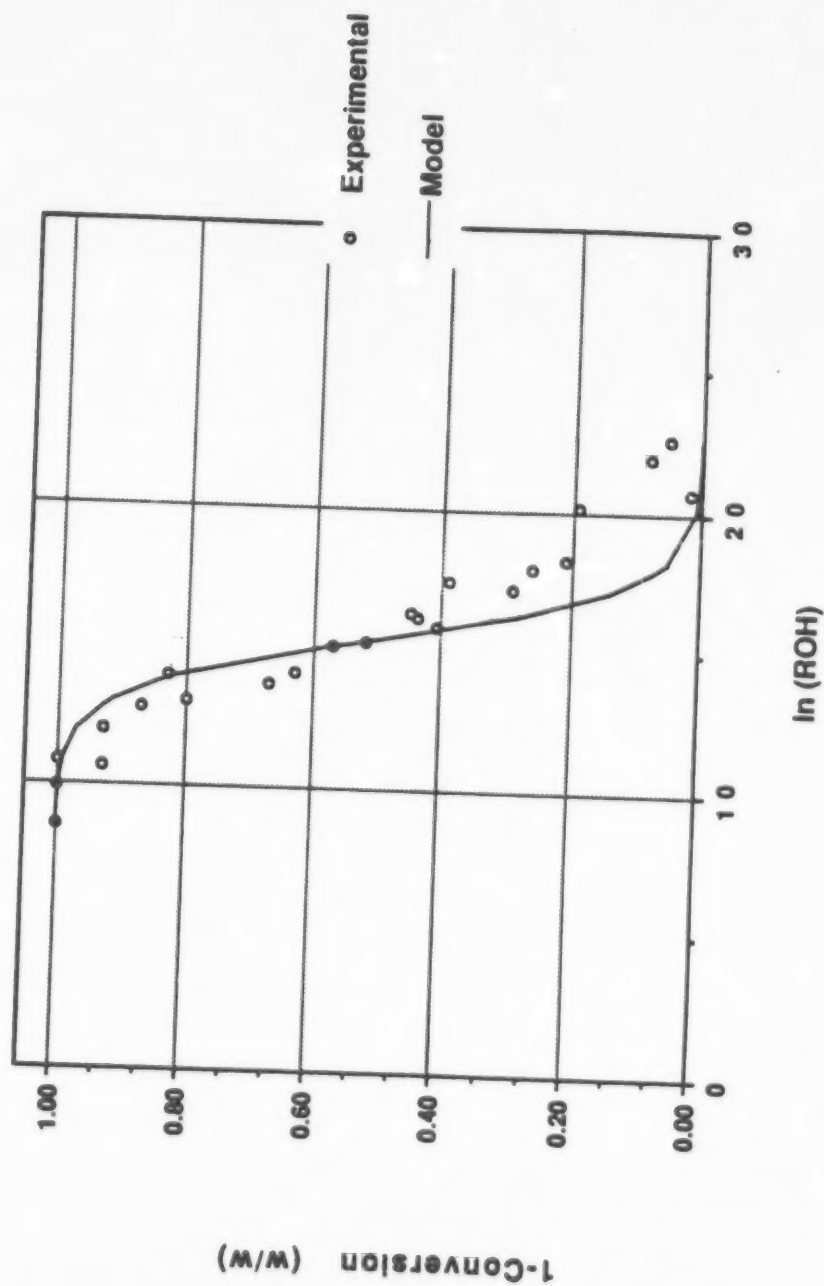


FIGURE 4
Data and Model for Alfa Hydrolysis
("Lumped" System Case)

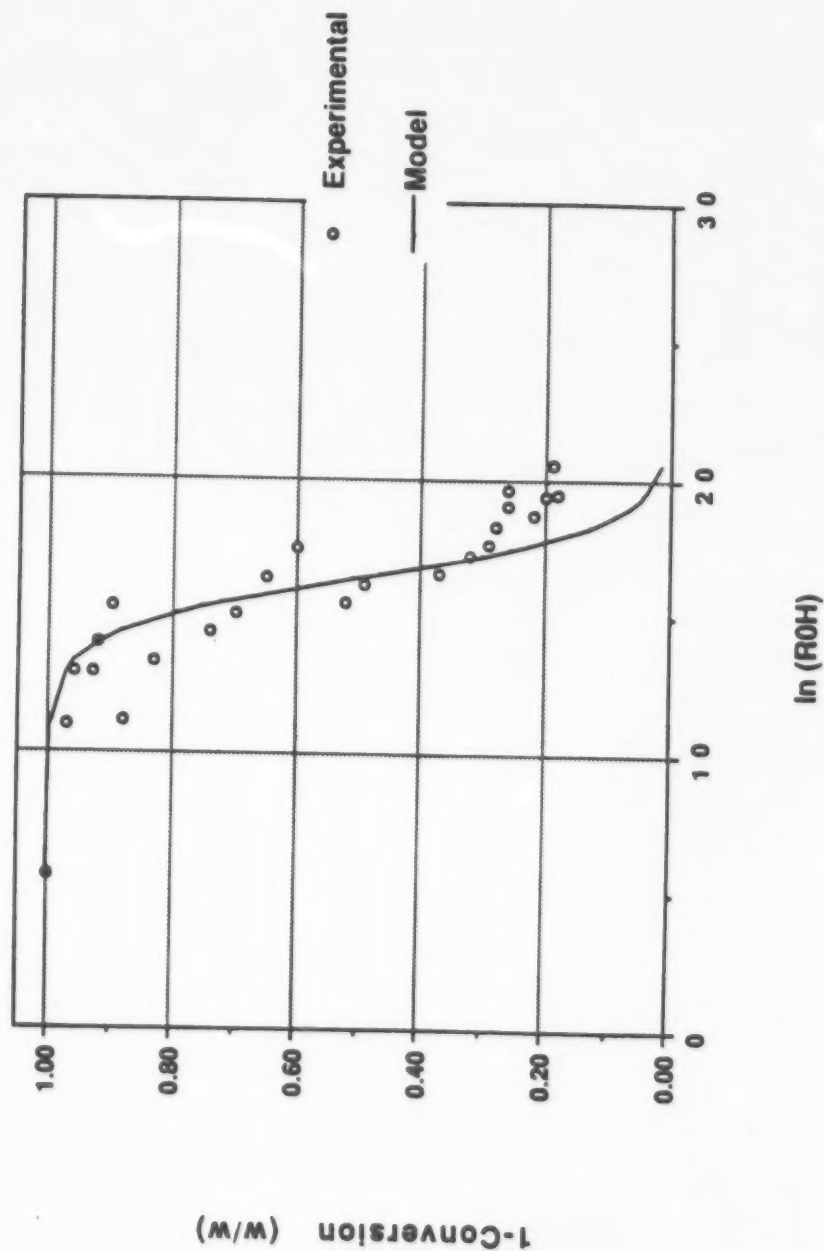


FIGURE 5
Data and Model for Populus tr. Hydrolysis
("Lumped" System Case)

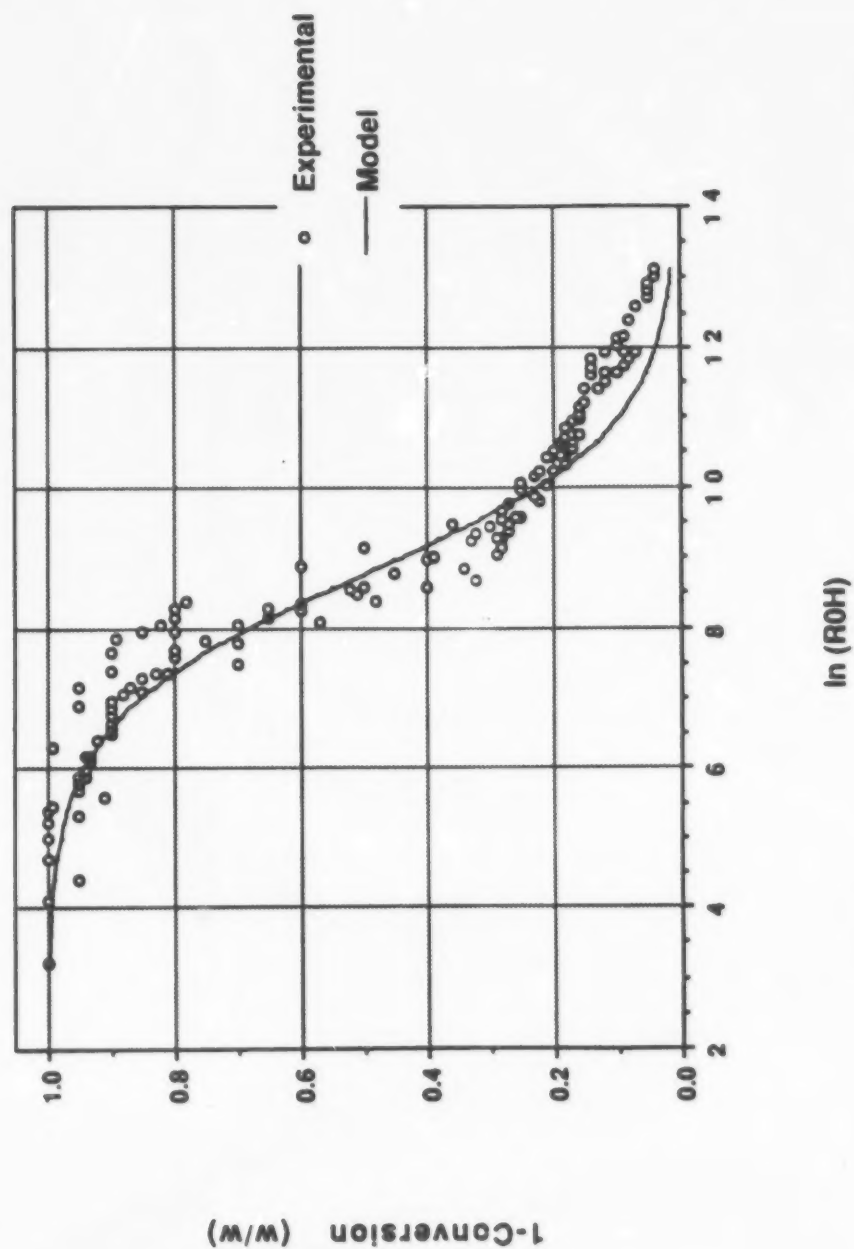


FIGURE 6
Data and Model from Betula pap. Hydrolysis
("Lumped" System Case)

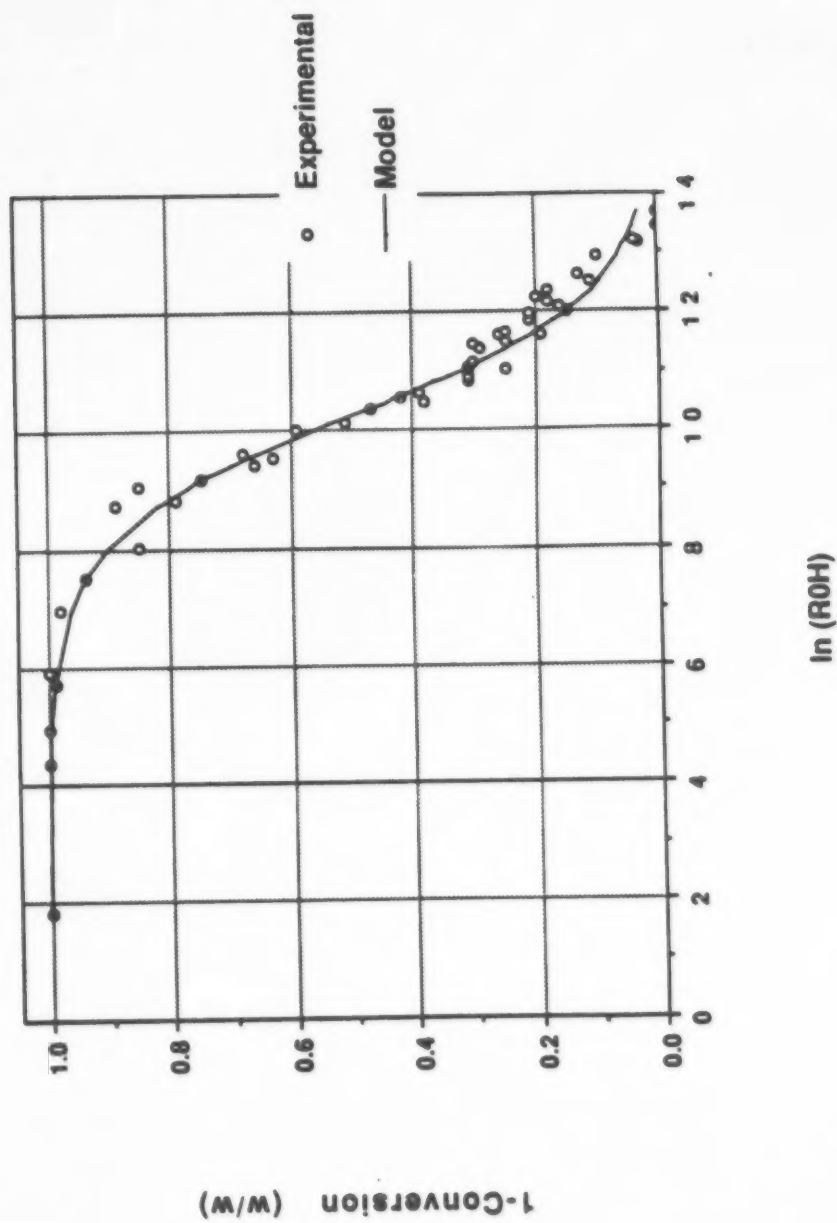


FIGURE 7
Data and Model from Corn stalks Hydrolysis
(The Continuous Distribution of Act. Energies Case)

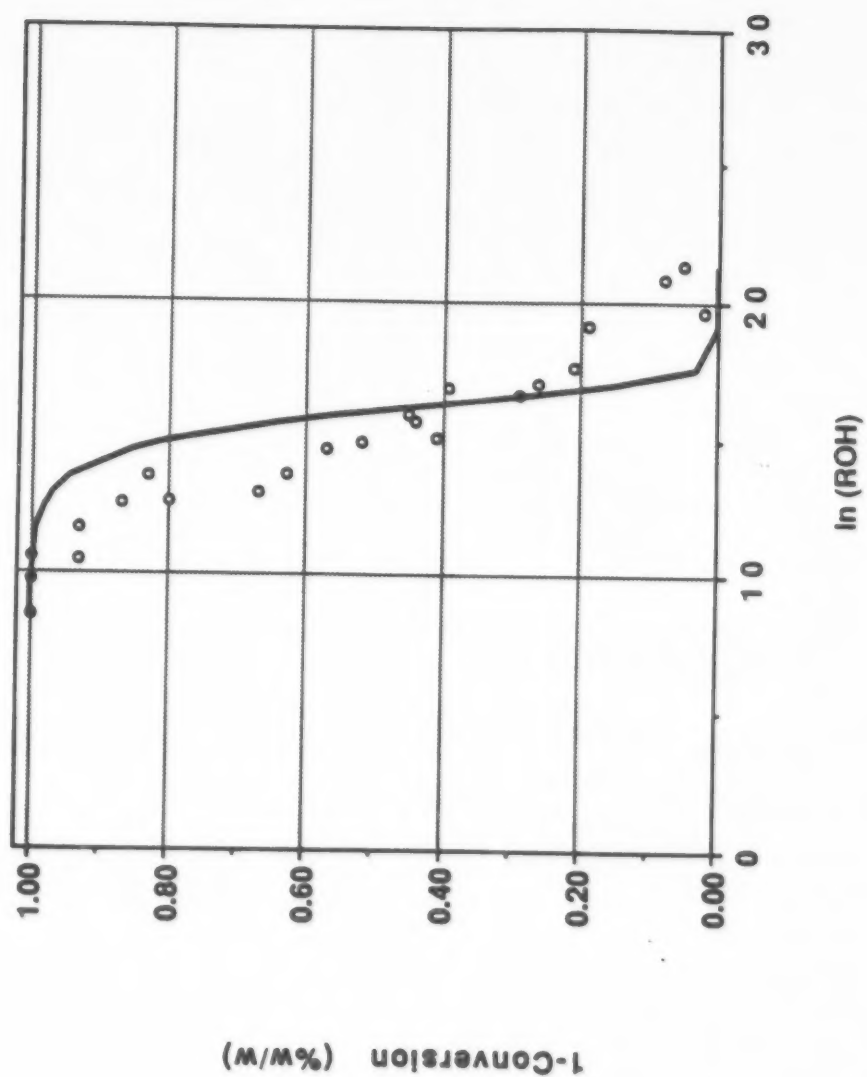


FIGURE 8
Data and Model from Stipa ten. Hydrolysis
(The Continuous Distribution of Act. Energies Case)

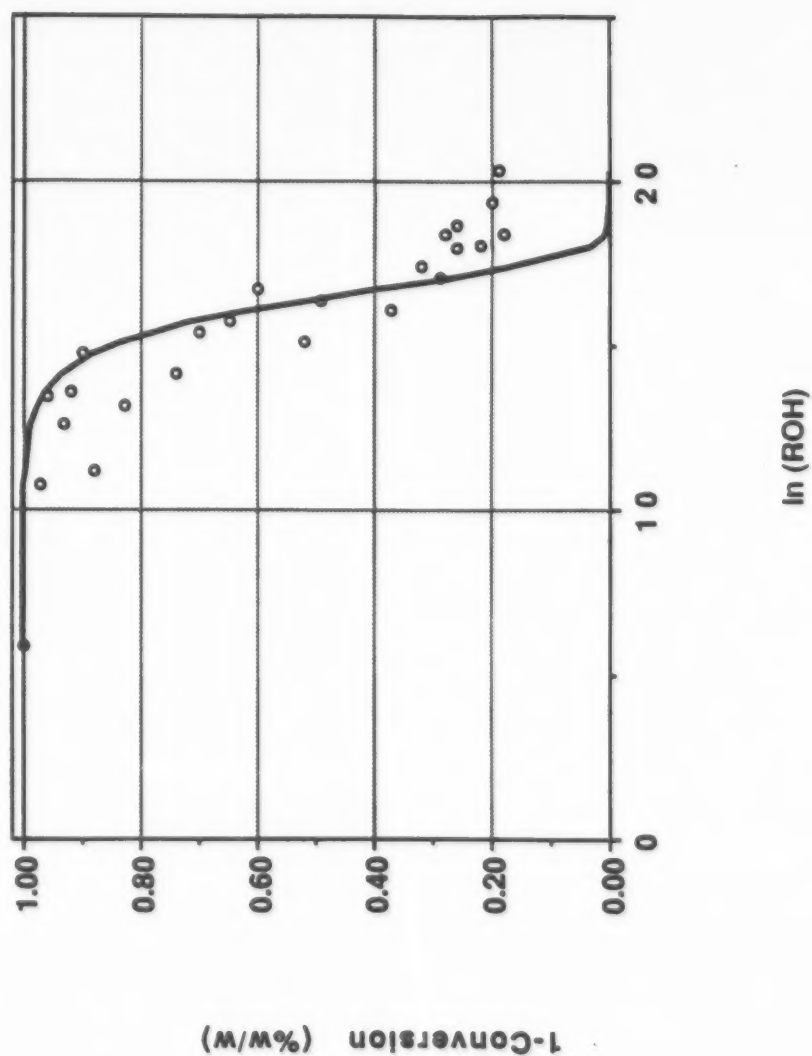


FIGURE 9
Data and Model from Populus t. Hydrolysis
(The Continuous Distribution of Act. Energies Case)

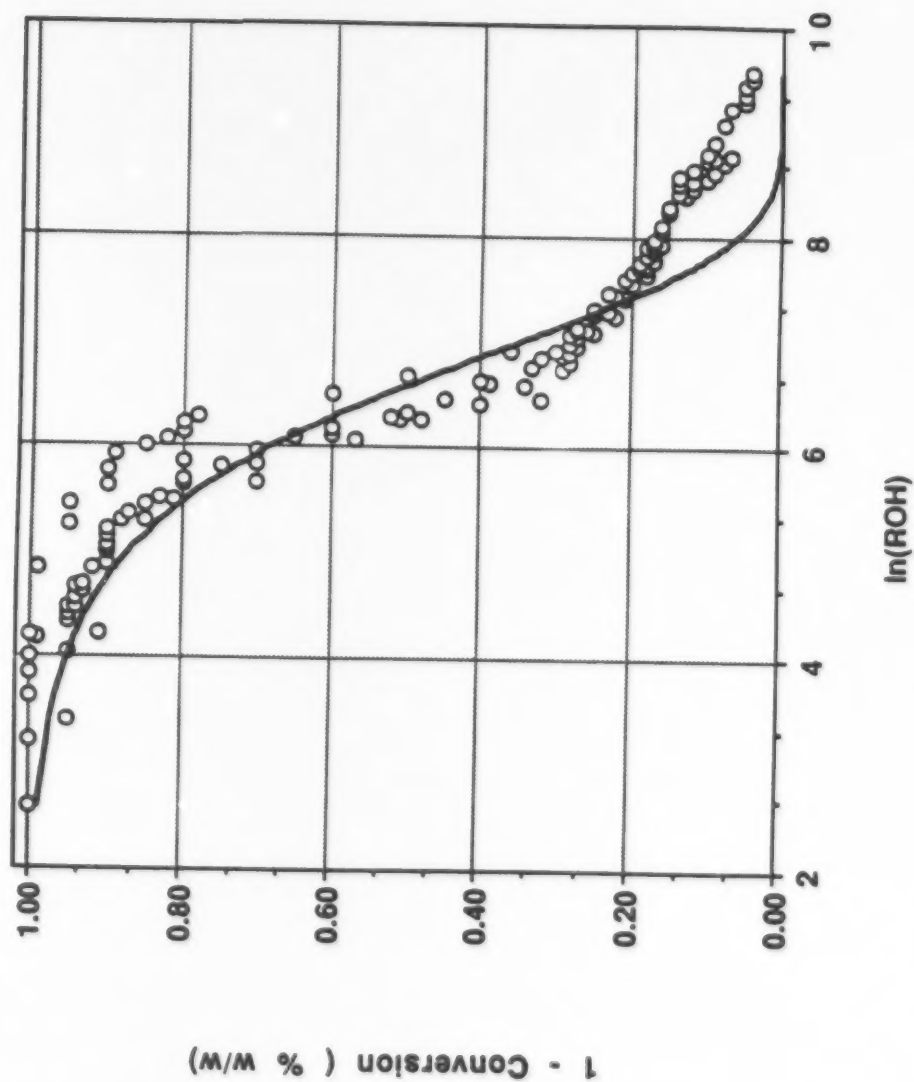


FIGURE 10
Data and Model from Betula p. Hydrolysis
(The Continuous Distribution of Act. Energies Case)

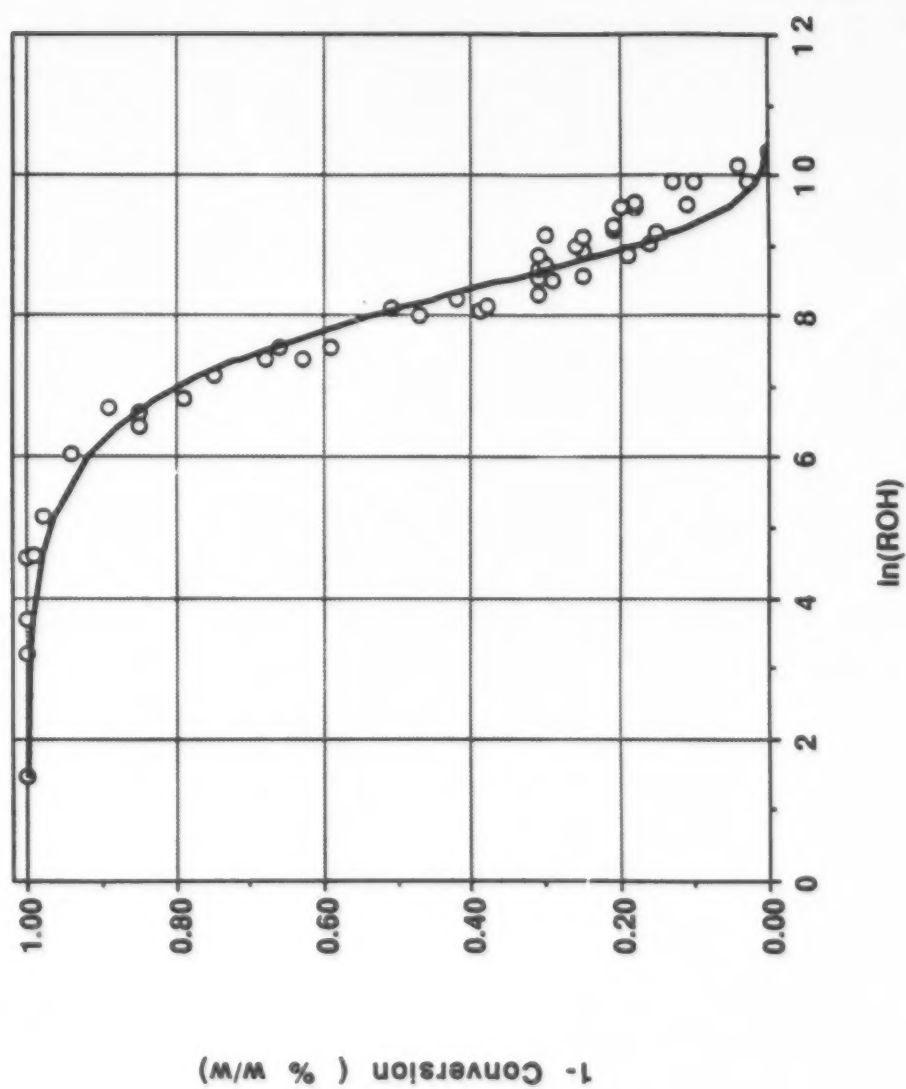


FIGURE 11
Sensitivity of λ vs ω
("Lumped System Case")

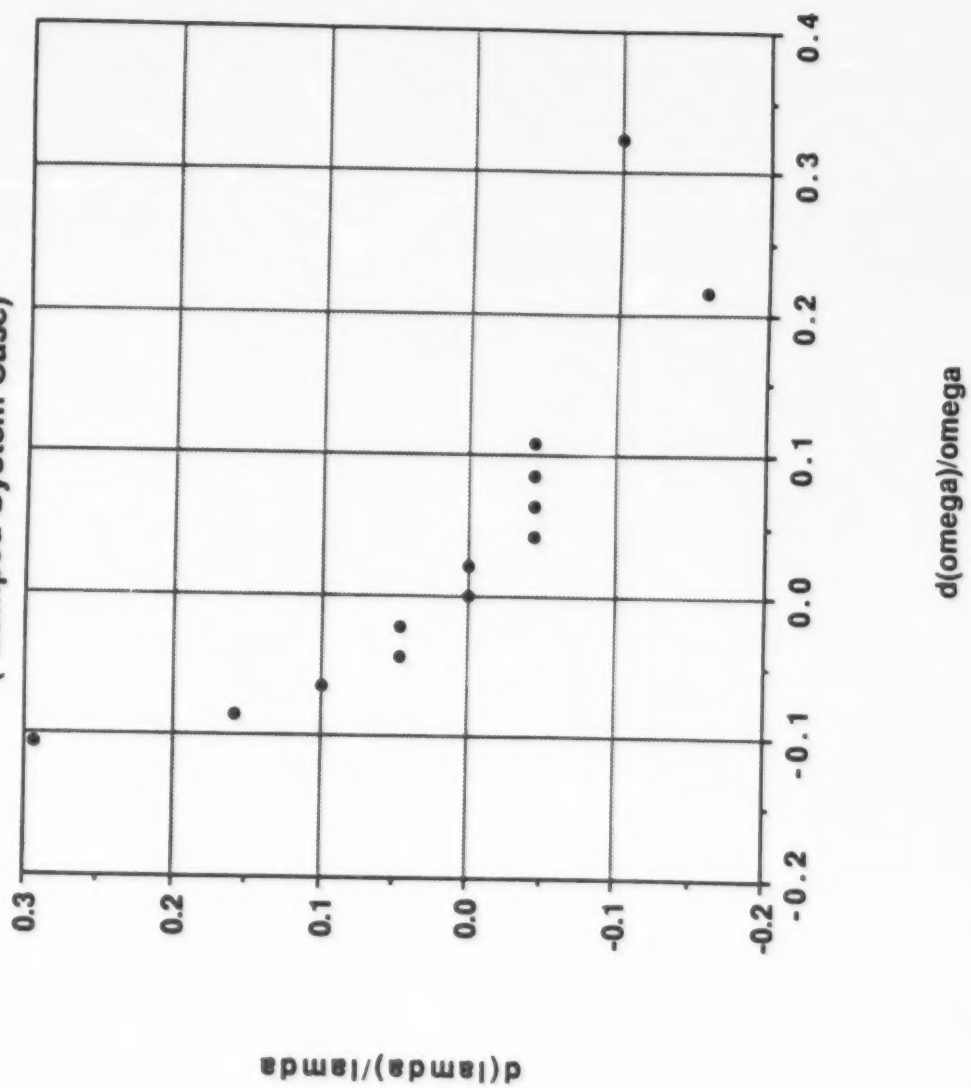


FIGURE 12. ORDERED EFFECTS FOR THE 2^3 FACTORIAL DESIGN

